SYNTHESIS OF meso-TETRAALKYLTETRABENZOPORPHINES

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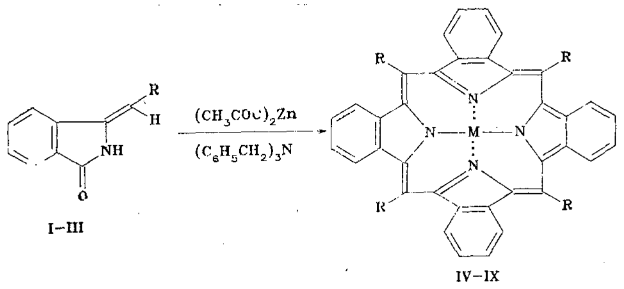
Stable complexes of zinc meso-tetralkyltetrabenzoporphines with tribenzylamine have been obtained by the template tetramerization of 3-R-methylenephthalimidines with zinc acetate in the presence of tribenzylamine or by the reaction of potassium phthalimide with the corresponding alkylmalonic acids. The structures of the compounds synthesized have been confirmed by their electronic absorption spectra, and in some cases also by their mass spectra.

The first representative of the meso-substituted tetrabenzoporphines — meso-tetraaryltetrabenzoporphines — were obtained by the reaction of phthalimide or potassium phthalimide with arylacetic acid or their alkali-metal salts in the presence of zinc acetate [1, 2]. Zinc meso-tetraphenyltetrabenzoporphines have also been obtained by the template tetramerization of 3-benzylidenephthalimidine in the presence of zinc acetate.

The tetramerization of the 3-R-methylenephthalimidines (I-III) (R = CH_3, C_2H_5, and C_3H_7) [3] with zinc acetate in the presence of tribenzylamine at 350-360°C for 30 min in an atmosphere of dry helium formed the zinc meso-tetraalkyltetrabenzoporphines (IV-VI), which have not previously been described in the literature, with yields of about 14%. In the absence of tribenzylamine, the final products (IV-VI) were not formed at all, or were detected in trace amounts. The catalytic role of the base probably amounts to increasing the mobility of the proton in the methylene group, which favors the occurrence of the reaction.



M=Zn, R=CH_3 (I, IV), C_2H_5 (II, V), C_3H_7 (III, VI), C_5H_{11} (VII), $C_6H_5CH_2$ (VIII);
M=H_2, R=CH_3 (IX)

The synthesis of meso-tetraalkyltetrabenzoporphines from phthalimide or potassium phthalimide with lower aliphatic acids and also with monoalkylmalonic acids (similarly to the synthesis of meso-tetraaryltetrabenzoporphines from phthalimide and arylacetic acids) leads to the desired product in low yields. For example, with n-amyl- and benzylmalonic acids the yields of the end products amount to 1.8 and 1.6%, respectively. Like their meso-aryl-substituted analogs, the zinc complexes (IV-VIII) synthesized possess higher solubilities than the unsubstituted zinc tetrabenzoporphine in a wide range of solvents (benzene, chloroform, ethanol, acetone, etc.), which permits their chromatographic purification to be carried out on alumina. The complexes synthesized have a high solubility not only in organic solvents but also in a polymeric matrix based on poly(methyl methacrylate) (PMMA).

Compounds (IV-VI) were isolated in the form of solvates with tribenzylamine. The formation of solvates with pyridine has been reported in the literature previously for the case of zinc complexes of tetrabenzoporphine [4, 5].

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TABLE 1. Characteristics of the Compounds (IV-IX) Synthesized

Compound	Electronic absorption spectrum, λ_{max}, nm (log ε), in chloroform	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IV	628 (4,80); 576 (3,82); 430 (5,33); 404 sh. (4,44); 626, 580, 429, 405 sh, 338 sh*	81,11 81,39	5,75 5,81	6,80 6,86	$C_{40}H_{28}N_4Zn \cdot 2(C_6H_5CH_2)_3N$	81,74	5,86	6,97	6
V	630 (4,95); 576 (3,83); 430 (5,43); 404 sh. (4,49)	80,63 80,94	5,33 5,36	6,52 6,76	$C_{44}H_{36}N_4Zn \cdot (C_6H_5CH_2)_3N$	80,19	5,90	7,19	10
VI	630 (4,97); 576 (3,97); 430 (5,51); 404 sh.(4,65)	80,54 80,68	6,36 6,32	7,35 7,32	$C_{48}H_{44}N_4Zn \cdot (C_6H_5CH_2)_3N$	80,49	6,36	6,80	14
VII	629 (4,40); 576 (3,55); 429 (4,92); 404 sh. (4,65)	—	—	6,33 6,54	$C_{56}H_{60}N_4Zn$	—	—	6,56	1,8
VIII	628 (4,76); 576 (3,92); 429 (5,35); 402 sh. (4,64)	82,55 82,60	4,92 4,85	5,94 5,70	$C_{64}H_{44}N_4Zn$	82,26	4,74	6,00	1,6
IX	662 (4,35); 614 (4,63); 606 (4,69); 600 (4,60); 562 (4,12); 432 (5,35); 418 (5,25); 390 (4,56)	86,29 86,15	6,63 6,53	8,71 8,69	$C_{40}H_{30}N_4 \cdot (C_6H_5CH_2)_3N$	85,81	6,02	8,20	60

*Electronic absorption spectra of compound (IV) in PMMA film (∿100 μ).

TABLE 2. Details of the Field-Desorption Mass Spectrum of meso-Tetramethyltetrabenzoporphine (IX) in % of the Maximum Peak*

m/z	854	839	824	763	749	672	658	581
I, %	100	20	19	68	77	39	96	34

*Emitter current 25 mA. The peaks with intensities ⩾15% are given.

The increased solubility of the compounds obtained is explained either by the presence of alkyl substituents noncoplanar with the macrocycle in the meso positions or by the formation of adducts with tribenzylamine, which introduces a steric hindrance to the crystal packing of the molecules.

The metal-free compound (IX) was obtained from the zinc complex (IV) by treating it with a chloroform solution of anhydrous hydrogen chloride at room temperature for 1 h. Elementary analysis, and also mass spectrometry, showed the presence of tribenzylamine in the molecule of compound (IX). The formation of stable adducts with nitrogenous bases (pyridine) has been reported previously for a number of metal-free tetraazaporphines [6]; this is the first time that this phenomenon has been observed for tetrabenzoporphines.

The electron-impact mass spectra of compound (IX) were recorded in the temperature interval of the inlet system of from 20 to 200°C, but they gave no information whatever about the structure of the substance, since it was possible to identify in them neither the peak of the molecular ion (which is characteristic for the electron-impact spectra of porphyrins [7-9]) nor the peaks of ions characteristic for the thermolysis products of the molecules under investigation. This is probably explained by the low volatility and thermal stability of this compound. Information on the composition and structure of these compounds was obtained from the field desorption (FD) mass spectra. The FD mass spectrum of compound (IX) is given in Table 2.*

As can be seen from Table 2, in the FD mass spectrum, the peak of maximum intensity is that of the protonated molecular ion (MH^+), confirming the empirical formula of compound (IX). In addition to the peak of the ion MH^+, the mass spectrum also contains the peaks of ions that permit the composition of the molecule under investigation to be established [10]. The formation of these ions can be explained both by the fragmentation of the molecular ion induced by the strong electric field and also by the thermal decomposition of the substance when the emitter is heated.

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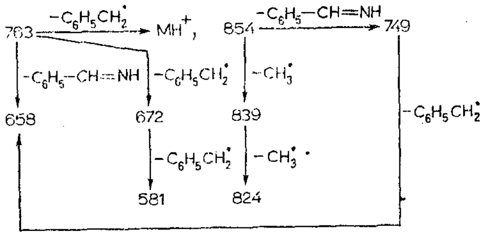
*We express our deep gratitude to V. L. Sadovskaya for recording the FD mass spectrum of compound (IX).

The 839 and 824* fragments are due to the successive loss of two methyl groups by the ion MH^+. Analysis of the relative intensities of the peaks of the other ions over a wide range of emitter temperatures permits the conclusion that their formation is due primarily to the thermal decomposition of the substance on heating. Nevertheless, these ions permit the reliable identification of the presence of a tribenzylamine fragment in the substance under investigation. The intensity of the peak of the 763 ion corresponds to the splitting out of a benzyl group from the molecular ion, and that of the 749 ion peak to the splitting out of a molecule of benzylideneamine. The formation of the main ions in the FD mass spectrum is shown in the scheme.



The electronic absorption spectra of the solutions of the compounds synthesized were measured in chloroform in the 220-750 nm interval. The introduction of alkyl substituents into the meso positions of the tetrabenzoporphine molecule has practically no effect on the positions of the Q and B bands. Thus, the Q bands of compounds (V, VI, and VIII) shift bathochromically in comparison with those of the unsubstituted compounds by only 1-2 nm, and the Soret band (B) shifts by 3-4 nm. In the metal-free compound (IX) the position and intensity of the doublet in the long-wave region (Q_1 and Q_2 bands) scarcely differ from those of the doublet of the unsubstituted compound (II), and the B_1 and B_2 bands are shifted bathochromically by 3 and 9 nm, respectively. The electronic absorption spectra were recorded in polymer films of PMMA. It was found that the electronic spectra of the compounds — for example, the zinc complex (IV) — in PMMA were practically identical with the spectra of these compounds in solutions.

EXPERIMENTAL

Electronic absorption spectra were recorded on Hitachi-356 and SF-4 spectrophotometers in rectangular quartz cells 10 mm thick with solutions having a concentration of $\sim 10^{-5}$ mM. The electron-impact mass spectra were recorded on an LKB-9000 instrument. Field-desorption mass spectra were recorded on a Varian MAT-311 instrument, the emitter current being varied in the interval of 20-40 mA.

Zinc meso-Tetramethyltetrabenzoporphine (IV). A mixture of 0.477 g (0.003 mole) of compound (I), 0.44 g (0.002 mole) of zinc acetate dihydrate, and 0.86 g (0.003 mole) of tribenzylamine was heated at 350-360°C for 30 min in a current of dry helium. Then the reaction mixture was chromatographed twice on alumina with elution first by chloroform and then by chloroform—petroleum ether (1:1), which yielded 0.054 g (6%) of the zinc complex (IV).

By a similar method, compounds (II) and (III) yielded the zinc complexes (V) and (VI) (Table 1).

Zinc meso-Tetrabenzyltetrabenzoporphine (VIII). The heating of 1.358 g (0.007 mole) of benzylmalonic acid, 1.16 g (0.006 mole) of potassium phthalimide, and 0.88 g (0.004 mole) of zinc acetate dihydrate at 360°C for 30 min followed by repeated chromatographic purification on alumina first with chloroform and then with chloroform—petroleum ether (1:2) yielded 0.0232 g (1.6%) of compound (VIII).

The complex (VII) was obtained by a similar method.

meso-Tetramethyltetrabenzoporphine (IX). Hydrogen chloride was passed at room temperature into a solution of 0.145 g (0.12 mmole) of the zinc complex (IV) in 20 ml of chloroform. Then the solution was washed repeatedly with ice water until the wash-waters were neutral, the aqueous layer was separated off, the organic layer was dried with sodium sulfate, the solvent was driven off, and the residue was purified on alumina with activity grade II (eluent: chloroform—petroleum ether (1:1)). This gave 0.061 g (60%) of compound (IX).

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*In the text and in the scheme, the numbers characterizing the ions show the ratio of mass to charge (m/z).

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SPATIAL STRUCTURE OF 3-ACYL-2-METHYLINDOLE OXIMES

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It has been established on the basis of the results of ^1H and ^{13}C NMR, UV, and IR spectroscopy that 3-acyl-2-methylindole oximes each exist in the form of a mixture of two isomers with a predominance of syn-s-trans form. The proportion of the anti form rises (to 25-35%) with an increase in the volume of the alkyl radical in the oxime grouping.

It has been shown previously that oximes of 2-unsubstituted 3-acylindoles exist mainly in the syn-s-trans form [1]. The aim of the present investigation was to determine the influence of a methyl group in position 2 of the indole nucleus on the spatial structure of the oximes.

The introduction of a methyl group also substantially changes the spectral properties of the 3-acylindole oximes. Thus, in the UV spectra of the 3-acyl-2-methylindole oximes two absorption bands are observed, at 225-231 and 280-283 nm, while in the spectra of the 2-unsubstituted oximes three absorption maxima appear, at 222-226, 257-259, and 283-290 nm. The disappearance of one of the absorption bands on the introduction of a methyl group into position 2 of the indole nucleus is apparently due to a disturbance of the coplanarity of the system and of the conjugation of the indole nucleus with the oxime grouping caused by steric hindrance between the methyl group and the radical in the oxime grouping.

The IR spectra of the oximes are unsuitable for answering the question of structure, since the bands of the C=N stretching vibrations in them lie in the 1610-1640 cm^{-1} region (Table 1) while the same band for unconjugated oximes is located at about 1640 cm^{-1} [2].

The PMR spectra of the 3-acyl-2-methylindole oximes show double sets of the signals of the protons of the methyl group in position 2, of the alkyl groups of the oxime residue, and of the hydroxy group (Table 2), which indicates the existence of two forms, due either to s-cis-trans or to syn-anti isomerism. A donor methyl group in position 2 changes the polarization and, consequently, the anisotropy of the C=N bond of the oxime grouping and causes a regular upfield shift of the signal of the 4-H proton as compared with 2-unsubstituted 3-acylindole oximes ($\Delta\delta$ 0.40-0.55 ppm). In spite of this, the signal of the 4-H proton remains in a weaker field than that for indole itself, which permits the assumption of the retention of the s-trans conformation and the ascription of the presence of two forms to syn-anti isomerism.

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