Synthesis and Properties of *meso*-Monophenyltetrabenzoporphine and Its Zinc Complex

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Abstract—*meso*-Monophenyltetrabenzoporphine and its zinc complex were synthesized starting from 3-(3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidenemethyl)-1*H*-isoindol-1-one. The effect of unsymmetrical *meso*-substitution on physical and spectral properties of the products is discussed. The results of quantum-chemical calculations suggest spatial distortion of the porphyrin macroring.

meso-Aryl-substituted tetrabenzoporphines have been studied for almost 20 years. First representatives of this group of compounds were reported in 1981 by Kopranenkov *et al.* [1] who synthesized the zinc complex of *meso*-tetraphenyltetrabenzoporphine (**I**) from phthalimide and phenylacetic acid in the presence of zinc acetate. The authors also assumed formation of partially *meso*-substituted products, i.e., zinc complexes of mono-, di-, and triphenyltetrabenzoporphines. Their formation may be explained by the presence in the reaction mixture of acetate ion as a source of methylene component. However, such compounds were neither isolated nor characterized.

Later on, the synthesis of *meso*-phenyl-substituted tetrabenzoporphines was studied in detail by Ichimura et al. [2]. By fusion of potassium phthalimide with zinc phenylacetate at 360°C for 1 h, the authors obtained a mixture of zinc complexes of meso-phenylsubstituted tetrabenzoporphines. Chromatographic separation of the mixture gave 3% of (meso-tetraphenyltetrabenzoporphinato)zinc(II) (I), 5.5% of (meso-triphenyltetrabenzoporphinato)zinc(II) (II), and 2% of (meso-diphenyltetrabenzoporphinato)zinc(II) (III). All the compounds were characterized by electronic absorption, ¹H NMR, and field desorption mass spectra. The formation of (meso-monophenyltetrabenzoporphinato)zinc(II) (IV) was also presumed [2], but this product was not detected. Compound IV was synthesized for the first time by Chang et al. [3] via condensation of phthalimide with sodium acetate in the presence of phenylacetic acid and a zinc salt, and electronic absorption spectrum of **IV** was recorded. However, the procedure described in [3] has considerable disadvantages, including low yield of the target product and difficulties in the separation of a mixture of approximately equal amounts of five products [(tetrabenzoporphinato)zinc(II) and *meso*-substituted derivatives **I**-**IV**]; among these, compounds **I**-**IV** are characterized by increased solubility.

Therefore, the goal of this work was to develop a new selective procedure for preparing *meso*-monophenyltetrabenzoporphine (**V**) and its zinc complex **IV** and to examine their physical and spectral properties. We previously reported [4] on the synthesis of **III** from 3-(3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidenemethyl)-1*H*-isoindol-1-one (**VI**) which is an intermediate product in the preparation of tetrabenzoporphines and is readily obtained by reaction of phthalimide with zinc(II) acetate dihydrate. Compound **VI** was also used to synthesize *meso*-monophenyltetrabenzoporphine (**V**) according to Scheme 1.

The reaction of compound VI with phenylacetic acid and zinc acetate yielded a mixture of three main products: (tetrabenzoporphinato)zinc(II) and compounds IV and III. In addition, small amounts of I and II were detected, presumably originating from partial thermal decomposition of VI. The mixture was separated by Soxhlet extraction of complexes I-IV with benzene and subsequent column chromatography. Compounds I, II, and III were identified by comparing their electronic absorption spectra with those reported in [2, 4]. meso-Monophenyltetrabenzoporphine (V) was obtained by demetalation of IV via treatment of its solution in tetrachloroethane with concentrated hydrochloric acid. The purity of IV and V was checked by TLC, and their structure was confirmed by elemental analyses and ¹H NMR, electronic absorption, and FAB mass spectra.

The mass spectrum of **IV** contained no ion peaks with m/z 724, 800, and 876, indicating the absence of impurities **I–III**. In the ¹H NMR spectrum of **IV**, sig-



Scheme 1.

nals from three *meso*-protons were observed in the region δ 12.5 ppm. Three groups of signals were present in the region δ 8.2–7.2 ppm. A triplet at δ 8.2– 8.0 ppm belongs to two *ortho*-protons of the *meso*phenyl fragment, and a multiplet at δ 8.0–7.8 ppm corresponds to three protons in the *meta*- and *para*positions. Protons of the isoindole fragments appear in the region δ 7.5–7.2 ppm (16H): eight protons in positions 3 and 6 give rise to a multiplet at δ 7.5– 7.4 ppm, and signals from those in positions 4 and 5 (8H) are observed at δ 7.4–7.2 ppm.

Compounds **IV** and **V** are dark blue crystalline substances which are better soluble in organic solvents (such as benzene, chloroform, and acetone) than unsubstituted tetrabenzoporphine owing to the presence of a bulky phenyl group.

The electronic absorption spectrum of V (see figure) considerably differs from the spectra of other *meso*-phenyl-substituted tetrabenzoporphines and resembles that of unsubstituted tetrabenzoporphine. The long-wave absorption band in the spectrum of V is split, which is also typical of tetrabenzoporphine. However, in the spectrum of the latter the long-wave absorption band is split into three components, while only two



Electronic absorption spectrum of meso-monophenyltetrabenzoporphine (V) in benzene.

components are observed for V. Also, the bands have different intensities. There are some differences in the mode of splitting of the Soret band. The splitting is stronger in the spectrum of V. As might be expected, the main absorption bands in the electronic absorption spectrum of V are red shifted relative to the corresponding bands of tetrabenzoporphine, though the shift is insignificant (2–3 nm). This may be due to positive inductive effect of the *meso*-substituent and reduced symmetry of molecular orbitals of nonplanar compound V.

We performed quantum-chemical calculations of molecule V by the AM1 semiempirical method with full geometry optimization [5]. Some results are given in the table.

According to the calculations, molecule V has in fact nonplanar structure. One of the isoindole fragments ($C^{12}C^{16}C^{17}C^{18}C^{19}C^{20}C^{15}C^{14}N^{13}$) is turned by an angle of more than 35° relative to the macroring plane. Obviously, this is due to the steric effect of the *meso*-phenyl substituent, which reduces the point symmetry group of the macroring to C_s .

Thus, we have developed a new method for synthesizing the zinc complex of *meso*-monophenyltetrabenzoporphine, which ensures higher yield of the target product and simpler purification procedure.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi UV-2000 spectrophotometer. The mass spectrum (fast atom bombardment in a *m*-nitrobenzyl alcohol matrix) was obtained on a Finnigan HSQ-30 mass spectrometer. The ¹H NMR spectrum was recorded on a Bruker WM-200 instrument (Autonomous University of Madrid, Spain).

3-(3-Oxo-2,3-dihydro-1*H***-isoindol-1-ylidenemethyl)-1***H***-isoindol-1-one (VI). A mixture of 16 g of**

phthalimide and 23 g of zinc(II) acetate dihydrate was placed in a quartz test tube; it was heated to 230°C and kept for 20 min at that temperature. After cooling, the melt was ground and washed in succession with a 10% solution of sodium hydroxide, water, 10% hydrochloric acid, and water again until washings became neutral. The product was dried and dissolved in acetone, and the solution was chromatographed on a column packed with alumina (activity grade II) using acetone as eluent. Yield 5.1 g (27%), mp 230 -232°C. The product is soluble in acetone, pyridine, DMF, and acetic acid and insoluble in water. Electronic absorption spectrum (pyridine), λ_{max} , nm (D): 357 (0.38), 515 (0.30), 550 (0.26). Found, %: C 74.40; H 3.70; N 10.19. C₁₇H₁₀N₂O₂. Calculated, %: C 74.45; H 3.67; N 10.21.

(meso-Monophenyltetrabenzoporphinato)zinc(II) (IV). A mixture of 1 g of VI, 1.36 g of phenylacetic acid, and 1.85 g of zinc(II) acetate dihydrate was placed in a quartz test tube. The test tube was heated to 350°C and kept for 25 min at that temperature. The melt was cooled, ground, and extracted with benzene in a Soxhlet apparatus. The extract was evaporated to dryness, the dark green powder-like residue was dissolved in benzene, and the solution was applied to a column packed with aluminum oxide (Brockmann activity grade II). The column was eluted with benzene-hexane (1:5), and a fraction containing a mixture of compounds I and II (according to TLC data) was collected. The subsequent elution with benzenehexane-acetone (1:5:2) gave a fraction containing compounds III and IV. This fraction was subjected to repeated chromatography on alumina using benzenehexane-ethyl acetate (1:10:2) as eluent. We thus isolated 0.08 g (10% with respect to initial compound VI, 45% of the overall amount of complexes soluble in benzene) of compound IV as a dark blue powder. $R_f 0.38$ (benzene, Silufol). The product is readily soluble in DMF, benzene, toluene, and acetone and insoluble in water and dilute aqueous acids and alkalis. Electronic absorption spectrum (benzene), λ_{max} , nm (log ε): 625 (4.61), 587 (3.82), 427.5 (5.17). ¹H NMR spectrum (CDCl₃), δ, ppm: 12.5 s (3H), 8.2-8.0 t (2H), 8.0-7.8 m (3H), 7.5-7.4 m (8H), 7.4-7.2 m (8H). Mass spectrum (FAB), m/z: 651.2 $[M + 3H]^+$, $(650.2 \ [M + 2H]^+, \ 649.2 \ [M + H]^+, \ 648.2 \ [M]^+, \ 647.2$ $[M - H]^+$, 572.1 $[M - C_6H_5]^+$. Found, %: C 78.12; H 3.85; N 8.45. C₄₂H₂₄N₄Zn. Calculated, %: C 77.60; H 3.72; N 8.62.

meso-Monophenyltetrabenzoporphine (V). Complex IV, 0.1 g, was dissolved in 10 ml of tetrachloroethane, 5 ml of concentrated hydrochloric acid was Bond lengths (d) and bond^a (∞) and torsion angles (τ) in the molecule of *meso*-monophenyltetrabenzoporphine (**V**) according to the results of AM1 calculations



^a Bond angles, deg: $C^{34}C^{1}C^{2}$ 126.1, $C^{4}C^{11}C^{12}$ 120.5, $C^{14}C^{21}C^{22}$ 125.6, $C^{24}C^{31}C^{32}$ 125.2.

added, and the mixture was stirred for 2 h. It was then diluted with water, and the organic phase was separated, washed with water, aqueous ammonia, and water again until washings became neutral, dried, and evaporated. The residue was dissolved in benzene, and the solution was chromatographed on a column packed with alumina (activity grade II) using benzene-hexane-ethyl acetate (1:5:1) as eluent. Compound V was isolated as a dark blue powder. Yield 0.08 g (71%). R_f 0.46 (benzene, Silufol). The product is readily soluble in DMF, benzene, toluene, and acetone and insoluble in water and dilute aqueous acids and alkalis. Electronic absorption spectrum (benzene), λ_{max} , nm (log ε): 665 (4.06), 607 (4.11), 598 (4.21), 565 (3.88), 472 (3.92), 432 (4.98), 417 (4.79), 398 (4.08). Found, %: C 86.28; H 4.81; N 9.46. C₄₂H₂₆N₄. Calculated, %: C 85.98; H 4.47; N 9.55.

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