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# DIMERIC COVALENTLY-BONDED ANALOGS OF TETRABENZOPORPHYRIN

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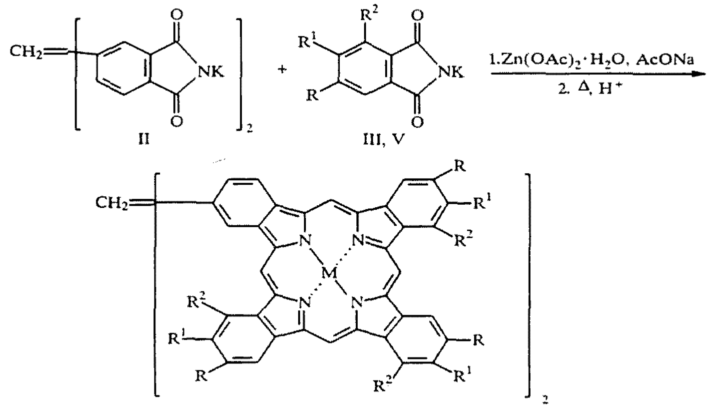
*Thermal condensation of a mixture of N-potassium imnides of diphenylmethane-3,3',4,4'-tetracarboxylic and phthalic acids in the presence of the acetates of sodium and zinc at 360-420°C gave the di-zinc complexes of methylene-bis-4,4'-(tetrabenzoporphyrin). This same scheme was used to prepare the di-zinc complex of methylene-bis-4,4'[tri-2,3-(1-phenylnaphtho)]benzoporphine. Acidic treatment of the di-zinc complexes gave the free bases. The synthesized compounds were characterized by electronic, $^1H$ NMR, and IR spectra.*

In recent times dimeric porphyrins with covalently-bonded bridges to the β-carbon atom of the pyrrole fragment or to the mesocarbon atom of the mesocarbon atom of he macrocycle have been widely studied [1, 2]. The dimeric porphyrins appear promising for application to the four-electron reduction of oxygen to water [3], photodynamic cancer therapy [4], models for the energy transfer process in the chlorophyll molecule [5], etc., while also notable is the superiority of their catalytic activity compared with the monomeric analog. The synthesis of dimeric phthalocyanines of similar structure was undertaken in a search for thermostabile catalysts [6]. Up to the present time, significant interest in these aspects of the dimeric analogs of the tetrabenzoporphines (TBP) has not appeared.

The method proposed earlier [7] for the synthesis of nonsymmetrical arenoporphines (NAP) by the thermal condensation of a mixture of imides of arene-o-dicarboxylic acids in the presence of acetates of sodium and zinc is set as the basis for preparing the dimeric TBP analogs.



I, IV, VI

$R = R^1 = R^2 = H$ (I, III, VI), $M = Zn$ (I), HH (VI); $RR^1$ = benzo-, $R^2 = C_6H_5$ (IV, V), $M = Zn$ (IV)

Thus, the di-zinc complex of methylene-bis-4,4'-TBP (I) was obtained by condensation of a mixture of the N-potassium-bis imide of diphenylmethan-3,3',4,4'-tetracarboxylic acid (II) with potassium phthalimide (III) in the presence of the acetates of sodium and zinc at 400-420°C over 1 h in a stream of helium with a yield of 22%. The dimeric NAP's were obtained analogously: the di-zinc complex of methylene-bis-4,4'-[tri-2,3-(1-phenylnaphtho)]benzoporphine (IV) was prepared by the mixed condensation of the N-potassium derivative of the bis-imide II with the imide of 1-phenylnaphthalin-2,3-dicarboxylic acid (V) [8] in the presence of the acetates of zinc and sodium.

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TABLE 1. Electronic Spectra of Dimeric Tetraarenoporphines

| Compound | Solvent | $\lambda_{max}$, nm (log $\varepsilon$) [Relative Intensity] |
|---|---|---|
| I | Chloroform | 624[0,36], 570[0,05], 424[1,0] |
| IV | Chloroform | 698[0,56], 680[0,59], 628 sh. [0,2], 534[0,08], 456[1,0] |
| VI | Pyridine | 662[0,14], 613[0,16], 607[0,2], 599[0,19], 558[0,06], 430[1,0], 415[0,84] |
|  | Con. $H_2SO_4$ | 656[0,24], 514[0,4], 472[0,11], 430[1,0], 392[0,45] |
| Zn-TBP | Pyridine | 628(5,11), 583(4,20), 433(5,60), 409(4,52)* |
| $H_2$-TBP | Pyridine | 662(4,01), 612(4,38), 607(4,40), 600(4,33), 568(3,83), 431(4,98), 416(4,90)* |

*From [10].

Compound I was convered into the free base of VI by passing gaseous HCl through a solution in concentrated $H_2SO_4$ at 40°C or in benzene at 20°C. Simultaneously with the dimeric TBP analogs I and IV, the cyclic complexes of the monomeric porphines, TBP and tetraz-2,3-(1-phenylnaphto)porphine, respectively, were formed in the synthesis process. They were easily separated from the dimers by chromatography on aluminum oxide.

Compound VI, in contrast to the non-metallic TBP's, was easily soluble in such strongly polar solvents as pyridine and DMF, and thus it was purified by repreciptation from concentrated $H_2SO_4$. The symmetrical and nonsymmetrical arenoporphyrin dimers obtained were inclined to form solvates [7, 9].

The structures of the dimers I, IV, and VI were confirmed by IR and $^1H$ NMR spectroscopy. Thus, the IR spectrum of compound I showed bands at 2922, 3026, 3051, and 3075 $cm^{-1}$, characteristic of the valence oscillations of aliphatic methylene bridges, and the spectrum of compound VI contained a wide non-structured band at 3200 $cm^{-1}$, related to the NH-valence oscillation of the iso-indole fragment.

In the $^1H$ NMR spectra of compounds I and IV, several signals for the protons of the methylene bridge with $\delta = 4.16$, 4.14, and 4.17, 4.14 ppm, respectively, were observed. The presence of several signals from the protons of the methylene bridge is connected, apparently, with the axial coordination of solvent molecules with the central metal atom. In the $^1H$ NMR spectrum of the free base of VI in DMSO-$d_6$, the signal for the NH proton was visible in the strong field region ($\delta > -3$ ppm). The respective internal intensities of the aromatic protons, the methylene protons, and the NH protons for the synthesized dimers were observed in good agreement with the calculated values and conclusively confirm their structures.

The electronic absorption spectra (EAS) of solutions of compounds I, III, and V were measured in the 350-750 nm region. Comparison of the EAS of compounds I, III, and their monomeric analogs [10] did not show any appreciable difference, although a narrowing of the half-width across bands $Q_1$ and $Q_2$ by ~ 100 $cm^{-1}$ was noted for compound III compared with the non-metallic TBP. The EAS of compound IV, the first representative of the dimeric NAP's, was characteristic of its monomeric analog. Thus the Q band occurs in the form of a doublet at 698 and 680 nm, and the Cope band is a single at 456 nm. All absorption bands in the EAS of dimer IV are displaced bathochromically with respect to their monomeric analogs [7], in which the Cope band is displaced 12 nm.

A general property of the EAS of these compounds is the hypochromic shift of the Q band with reference to the Cope band compared with their monomeric analogs which earlier was noted for the dimeric porphine [11].

Both in acidic and basic media the EAS of the non-metallic compound VI was transformed analogously with the metallocomplexes as a result of the formation of the more highly symmetrical dicationic (because of the protonation of the central nitrogen atoms) and the dianionic (because of the deportonation of the central imino groups) forms.

Increasing the solubility of the zinc complexes of I and IV allows their existence in a polymeric matrix (for example, polymethylmethacrylate), the EAS of which are close to those in organic solvents.

## EXPERIMENTAL

The EAS of solutions of the synthesized compounds was obtained with an Hitachi-356 and Unicam-700 instruments on solutions of $10^{-5}$-$10^{-3}$ M. The $^1H$ NMR of the compounds were recorded with a Bruker MS-360 spectrometer ($C_5D_5N$,

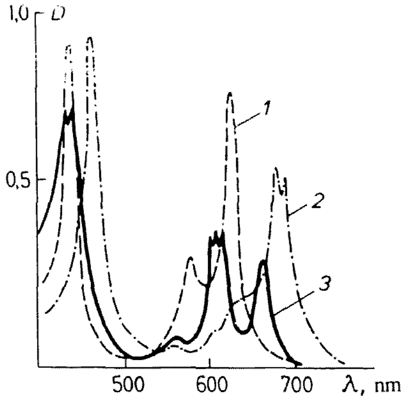

Fig. 1. Electronic Spectra of Compounds I (1) and IV (2) in Chloroform and IV (3) in Pyridine.

TMS internal standard, 90°C), and also with a Bruker VP-200 SU instrument (DMSO-$d_6$, TMS internal standard, 80°C). The IR spectra were determined with a Perkin–Elmer 598 in KCl tablets. Chromatographic purification and monitoring of purity were carried out on neutral aluminum oxide, activity Brockmann Grade II.

Elemental analysis data corresponded with the calculated values.

**Diphenylmethane-3,3′,4,4′-tetracarboxylic Acid (VII).** A mixture of 42 g (0.13 mole) of the dianhydride of benzophenone-3,3′,4,4′-tetracarboxylic acid, 34 ml of 57% HCl and 34 g (1.1 mole) of finely-pulverized red phosphorus was stirred for 90 h at 110-130°C. To the reaction mass was added 20% NaOH to pH 8, the solution was filtered, and the filtrate acidified with conc. HCl to pH 4 and the precipitate was removed. The solvent was evaporated to give 25 g (55%) of acid VII, mp 286-289°C (from DMF), Lit. [12], mp 290°C.

**Dianhydride of Diphenylmethane-3,3′,4,4′-tetracarboxylic acid (VIII).** A solution of 16.7 g (0.05 mole) of acid VII in 120 ml of acetic anhydride was boiled for 1 h, cooled, and the precipitate was filtered to give 11.1 g (70%) of anhydride VIII, mp 242-244°C (from acetic anhydride). Lit. [12], mp 242-244°C.

**Diimide of Diphenylmethane-3,3′,4,4′-tetracarboxylic Acid (II).** A mixture of 11.1 g (0.035 mole) of anhydride VII, 55 g (0.7 mole) of ammonium acetate and 170 ml of acetic acid was boiled for 3 h, cooled, and the precipitate was separated to give 11.1 g (~100%) of imide II, mp 374-375°C (from acetic anhydride). Lit. [13], mp 375°C.

**Dipotassium Derivative of Bis-imide II.** The bis-imide II (3 g 9.4 mmoles) was dissolved with heating in 1.3 liters of ethanol, then treated with 1.12 g (20 mmoles) of KOH in 10 ml of 75% ethanol. The mixture was concentrated to 150 ml, cooled, and the precipitate was separated to give 3.65 g (98%) of the dipotassium derivative of bis-imide II.

**Di-zinc Complex of Methylene-4,4′-(tetrabenzoporphine) (I).** A mixture of 0.1 g (0.1 mmoles) of bis-imide II, 2 g (0.01 mole) of potassium phthalimide, 0.5 g (2.5 mmoles) of zinc acetate dihydrate and 1 g (12 mmoles) of sodium acetate was kept for 1 h at 400-420°C in a stream of helium. The mixture was then pulverized, washed with water, HCl (1:1), $NH_4OH$ (1:1), and ethanol. The residue was dissolved in pyridine, transferred to a column, and eluted with a mixture of benzene–pyridine, 50:1, then hexane–ethyl acetate–benzene–pyridine, 5:1:4:0.1, to give 0.08 g (22%) of complex I with $R_f$ 0.4 (Hexane–ethyl acetate–benzene–pyridine, 5:3:17:0.25).

**Di-zinc Complex of Methylene-bis-4,4′-[tri-2,3-(1-phenylnaphtho)benzoporphinel (IV).** A mixture of 0.3 g (1 mmole) of N-potassium bis-imide II, 1.5 g (5 mmoles) of N-potassium imide of 1-phenylnaphthaline-2,3-dicarboxylic acid [8], 1 g (4.6 mmoles) of zinc acetate dihydrate and 2 g (24 mmoles) of sodium acetate was kept for 1 h at 380-420°C in a stream of helium. The reaction mixture was worked up analogously with compound I. The residue, was dissolved in pyridine, transferred to a column and eluted with a mixture of benzene–pyridine, 50:1, then benzene–hexane–triethylamine, 5:5:1, to give 0.23 g (13%) of compound IV with $R_f$ 0.28 (chloroform).

**Methylene-bis-4,4′-(tetrabenzoporphine) (V).** A solution of 0.11 g (1 mmole) of dimer I in 40 ml of conc. $H_2SO_4$ was kept for 1 h at 40°C. The reaction mixture was poured onto ice, neutralized with conc. $NH_4OH$. The precipitate was separated by centrifugation, washed with water and ethanol, dried, and chromatographed on a column of aluminum oxide in pyridine to give 0.07 g (65%) of compound V, IR spectrum: 3420 $cm^{-1}$ (OH bond).

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