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NITRO-SUBSTITUTED PORPHYRAZINES

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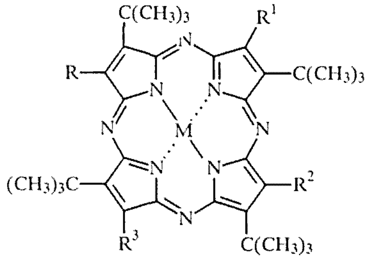
This nitration of tetra(tert-butyl)porphyrazine and its metal complexes with different nitrating agents has given their mono-, di-, tri-, and tetra-nistro-derivatives; the metal complexes have also been obtained by the metallation of the corresponding metal–free nitroporphyrazines. The structure of the synthesized compounds has been confirmed by electron and mass spectra, and by PMR spectra.

The porphyrazine molecule, which possesses an increased resistance toward oxidation in comparison with the porphyrins and even the phthalocyanines [1], is of interest for the synthesis of compounds used as fast pigments, as catalysts in different reactions, etc. Their stability can be further improved by introducing electron-acceptor substituents (for instance, nitro groups) into the porphyrazine macrocycle. Nitro–derivatives of porthyrazine have not been described in the literature; our attempts of their synthesis starting from the 1-aryl-2-nitro-maleonitriles [2] showed that the latter are easily isomerized at the reaction conditions used with the formation of the unreactive trans–isomers.

With the aim of preparating nitro–substituted porphyrazines, we studied the nitration of tetra(tert-butyl)porphyrazine (I) and of its cobalt (II) and copper (III) complexes. The nitrating agents used were solutions with different concentrations of fumic nitric and acetic acid, as well as nitronium fluoborate in sulfolane and dinitrogen tetroxide in hexane. In the nitration of the metal–free compounds I with a mixture of fuming nitric acid and glacial acetic acid (1:2) at 20-25°C, a mixture is formed in 3-5 min of di- (IV), tri- (V), and tetranitro-tetra(tert-butyl)porphyrazine (VI) with the yields 25.5, 23, and 36.5% respectively; two more strongly polar compounds (a "green" and a "blue") are also formed. Products of mononitration have not been observed at these conditions. By extending the reaction to 2 h, a mixture of compounds V and VI is formed with the yields 5 and 72%. Mononitro-tetra(tert-butyl)porphyrazine (VII) was obtained by the nitration of compound I with only at 2% solution of nitric acid in acetic acid with a yield of 6.5%, in mixture with the dinitro derivative IV and the initial compound I (70%).



IV-XV

VII M = 2H, R = NO_2, $R^1 = R^2 = R^3$ = H; IV M = 2H, XI Co, XIII Zn, $R = R^1 = NO_2$ or $R = R^2 = NO_2$,
$R^2 = R^3$ = H; V M = 2H, IX Cu, XII Co, XIV Zn, $R = R^1 = R^2 = R^3 = NO_2$

The nitration of the porphyrazine I with fuming nitric acid in glacial acetic acid (1:2) proceeds more readily than with octa-substituted porphyrin and chlorin [3]. At these conditions octaethylporphyrin forms after 1.5 min the monosubstituted product with a yield of 92%, after 30 min mainly the dinitro derivative; a small amount of the trinitro derivative appears only after 3 h. No product of tetra-substitution was observed at all.

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TABLE 1. Electron Absorption Spectra of Nitroporphyrazines (IV-XV) in Chloroform

Compound	t-Bu$_4$(NO$_2$)$_n$-porphyrazines	λ_{max}, nm (log ε) or [relative intensity]
IV	Metal-free, n = 2	623(4,82), 593(4,02), 556(4,61), 526sh (4,17), 338(4,83) 617[1,0], 591[0,17], 549[0,67], 520[0,17], 331[0,96]*
V	Metal-free, n = 3	618(4,81), 569(4,64), 528sh(4,11), 337(4,82) 612[1,0], 582sh[0,21], 555[0,74], 518sh[0,28], 332[1,03]*
VI	Metal-free, n = 4	632(4,87), 604(4,01), 563(4,71), 530sh(4,17), 341(4,85) 623[1,0], 591[0,2], 564[0,28], 545[1,09], 514sh[0,32], 337[1,04], 321[0,79]*
VII	Metal-free, n = 1	615(4,79), 574(4,64), 536sh(4,18), 332(4,81) 610[1,0], 555[0,69], 514[0,29], 330[1,02]*
VIII	Cobalt, n = 4	577(4,84), 529sh(4,36), 317(4,68) 576[1,0], 528sh[0,48], 315[1,05]*
IX	Copper, n = 3	594[1,0], 576[0,93], 548[0,29], 534sh[0,23], 338[0,87]
X	Copper, n = 4	588[1,0], 536[0,2], 338[0,53]
XI	Cobalt, n = 2	573(4,88), 524sh(4,41), 336sh(4,79), 317(4,68)
XII	Cobalt, n = 3	568[1,0], 524sh[0,42], 316[1,33]
XIII	Zinc, n = 2	598[1,0], 548sh[0,27], 337[0,7]
XIV	Zinc, n = 3	608[1,0], 592[0,94], 543sh[0,3], 333[0,87]
XV	Zinc, n = 4	602[1,0], 584[0,9], 538sh[0,2], 338[0,78]

*In hexane.

The nitration of the cobalt complex II with the same nitrating agent gave in 3 min only the cobalt tetranitrotetra(tert-butyl)porphyrazine (VIII) with a yield of 51.5%; in the case of the copper complex III a mixture of the copper tri- (IX) and the tetranitrotetra(tert-butyl)porphyrazines is formed at these conditions with yields of 13.5 and 45%.

Another approach to the synthesis of metal porphyrazine complexes is the metallation of the corresponding metal-free compounds. Thus, the cobalt complexes of di- (XI), tri- (XII), and tetranitrotetra(tert-butyl)porphyrazine (VIII) were obtained from the porphyrazines IV-VI and cobalt II chloride in boiling trichlorobenzene in the presence of catalytic amounts of ammonium molybdate with yields of 21.67 and 92% respectively. These values indicate that an increase in the acidity of the imino groups in the given series increases the yield of the metallation reaction. In the same way the metal–free compounds IV and VI give by refluxing with zinc acetate for 2-3 min the zinc complexes of di- (XIII, tri- (XIV), and tetranitro-tetra(tert-butyl)porphyrazine (XV) with virtually quantitative yields.

The nitration of the porphyrazines I-III with the nitrating mixture is probably based on an electrophilic mechanism with the participation of the nitronium cation. Analogous results were obtained with nitronium fluoborate as the nitrating agent.

The nitration of compound I is probably based on a radical mechanism with dinitrogen tetroxide; nevertheless, it leads to the formation of the same products, although in a different ratio. Thus, the nitration of compound I by this method at room temperature for 10 min gave a mixture of compounds V (3%) and V (5%); increasing the duration of the reaction to 1 h a mixture of compounds IV (4%), V (9%), and VI (1.5%) was obtained, together with a considerable amount of breakdown products. The data of the quantum–chemical calculation of the electron density of the porphyrazine molecule [4] are in agreement with our experimental results.

The synthesized complexes represent–crystalline substances, colored in different shades of violet; they are readily soluble in a wide range of organic solvents (hexane, benzene, chloroform, etc.). This simplifies the chromatographic purification and also makes it possible to carry out our spectroscopic investigations in low-polarity solvents. Some complexes (for instance, the zinc complexes XIV-XVI) possess an intensive red fluorescence, in spite of the presence of nitro groups in the molecule, which usually have a quenching effect. Some compounds have well defined melting points: compound V 270-

272°C, XII 62-64°C, and IV 323-325°C. The nitro compounds V and X form relatively strong solvantes with hexane and benzene respectively.

The IR spectra of the nitro-derivatives IV-VII taken in KBr tablets, show bands in the regions 1363-1386 and 1515-1558 cm^{-1}, which are characteristic for symmetrical and asymmetrical stretching vibration of the nitro groups [5], as well as bands in the region 835-860 cm^{-1}, characteristic for C–N vibrations. An increase in the number of nitro groups in the porphyrazine molecule shifts the streching-vibration bands of the nitro groups to the high-frequency region; the tert-butyl groups appear as triplets at 2870-2990 cm^{-1}. The IR spectrum of compounds IV-VI in KBr tablets contain two bands in the high-frequency region: a diffuse band at 3060-3270 cm^{-1} and a narrow band at 3295-3305 cm^{-1}, assigned to the vibrations of combined and free N–H groups. The IR spectrum in carbon tetrachloride contains only the second band, while the compound VI has only the narrow single band of the free NH groups at 3295 cm^{-1}. The IR spectra of the "green" and "blue" compounds are similar to the spectrum of the tetranitro derivative VI; however, they contain some differences. Thus, the "blue" spectrum contains additional bands at 1268 and 1665 cm^{-1}, which are tentatively assigned to vibrations of the ONO and ONO_2 groups [5]. Their presence correlates with the explosive properties of these compounds, manifested when melted and in attempts to perform mass-spectrometric analysis. The labile nature of these compounds prevented the acquisition of reliable elemental analysis data; however, the presence of these groups indicates that other processes also take place besides nitration.

The PMR spectra of di-and trinitrosubstituted compounds IV and V in deuterochloroform at 20-25°C show in the region of N–H protons doublets at −1.66, −1.80, and −1.76, −1.88 ppm respectively, the ratio of which does not change in the interval from 20 to 100°C. This is evidently due to the appearance of individual randomers, characterized by different mutual distribution of the tert-butyl groups, not due to NH-tautomerism.

When introducing nitro groups into the molecule of the metal-free compound I, a bathochromic shift of the longwave doublet (Q_1 and Q_2) is observed; the largest shift of the Q_1 band (to 12 nm) is obtained for the tetranitroporphyrazine VI and of the Q_2 band (to 27 nm) for the mononitroporphyrazine VII (see Table 1). In the spectrum of the metal complexes these differences are less pronounced. In the zinc porphyrazine complexes XIV and XV the band is split into two, which is probably due to different randomers.

The electron-acceptor character of the nitro groups affects the mobility of the NH-protons in the metal-free porphyrazine. Thus, in distinction from the unsubstituted analog, the nitroporphyrazines V and VI form dianionic forms in polar solvents (DMF, DMSO) even without the addition of a base. It has also been noticed that the presence of nitro groups in the molecule of the metal-free compounds and in their metal complexes increases considerably their oxidation stability. This is of interest for the creaction of effective catalysts on their basis, primarily for processes for the oxidation of different organic substrates.

EXPERIMENTAL

The progress of the reaction and the purity of the separated compounds was controlled by TLC on Silufol UV-254 plates. The electron absorption spectra of the synthesized samples were taken on Hitachi-356 and SF-4 spectrophotometer in rectangular quartz cells with a thickness of 10 mm; the concentration of the solutions was $\sim 10^{-5}$ M. The electron impact mass spectra were recorded on a Varian MAT CH-6 mass spectrometer; the ionization energy of the electrons was 70 eV. Fragment peaks were recorded, the intensity of which was higher by 2% than the maximum molecular ion. The IR spectra were obtained on an UR-20 spectrometer, V_{ret} 64/4, using Kbr tablets or a solutions in CCl_4. The PMR spectra were determined in $CDCl_3$ with hexamethyldisiloxane as internal standard on a Tesla NMR Spectrometer, model BS-487/80 MHz. The elemental analysis data of the synthesized compounds agreed with the calculated values.

Nitration of Tetra(tert-butyl)porphyrazine (I). A. A solution of 0.5 g (0.93 mmole) of compound I (R_f 0.48, benzene) [6] in 30 ml glacial acetic acid is treated in one lot with a mixture of 40 ml fuming nitric acid (d = 1.5) and 40 ml glacial acetic acid, precooled to 0°C. The coloration of the reaction mass changes from violet to dark green. The mixture is stirred for 3-5 min, poured on 500 ml water with ice, and slowly neutralized with 10% Na_2CO_3. The dark-blue precipitate formed is filtered off, washed on the filter water (3 × 250 ml), and dried at room temperature.

The technical product obtained (0.6 g) is dissolved in 20 ml chloroform and transferred to a chromatographic column, packed with silica gel (350 × 28 ml). The column is eluted consecutively with hexane and benzene–hexane, 1:1, collecting three fractions: 1) 0.143 g (23%) trinitro- compound V, R_f 0.65 (benzene–hexane, 2:1), mp 270-272°C; 2) 0.243 g (36.5%)

tetranitroderivative VI, R_f 0.47 (benzene–hexane, 2:1), mp 360°C; 3) 0.121 g (25.5%) dinitro-tetra(tert-butyl)porphyrazines (IVa, b) (probably a mixture of position isomers of the nitro groups), R_f 0.25 (benzene–hexane, 2:1), mp 323-325°C.

Besides this, two strongly polar substances (a "green" and a "blue") with R_f 0.27 and 0.94 (ethyl acetate) respectively, remain at the starting line of the chromatographic column; their separation is described below. When the duration of the reaction is extended to 30 min, an exhaustive nitration to the tetranitro-derivative VI takes place (yield 72%), accompanied by an increased yield of the strongly polar products.

B. A solution of 0.20 g (0.37 mmole) of compound I in 15 ml sulfolane is treated with 0.05 g (0.37 mmole) nitronium fluoborate. The reaction mass is kept 20 min at room temperature, poured on 250 ml water, and neutralized with 20 ml 10% Na_2CO_3. The precipitate formed is filtered off, washed on the filter with water to a neutral reaction of the wash waters, and dried in air at room temperature. Obtained is a mixture of the di-, tri-, and tetranitro-derivatives IV-VI (0.236 g) which is dissolved in 15 ml benzene and chromatographed on silica gel by eluting with benzene–hexane 1:1. Three fractions are collected: 1) 0.127 g (51%) of compound V, 2) 34 mg (12.7%) of compound VI, and 3) 32 mg (13.7%) of compound IV.

C. A solution of 0.50 g (0.925 mmole) of compound I in 15 ml hexane is treated with a solution of 1.0 g (10.9 mmole) N_2O_4 in 5 ml hexane and kept at room temperature for 1 h. The reaction mass is purged with helium to remove the excess nitrogen oxides and chromatographed on silica gel with benzene–hexane, 1:1. Three consecutive fractions are collected: 1) 60 mg (9%) of compound V, 2) 25 mg (4%) of compound IV; and 3) 0.01 g (1.5%) of compound VI. Besides this, blue polar products are formed in this reaction.

Mononitrotetra(tert-butyl)porphyrazine (VII). A solution of 0.2 g (0.372 mmole) of compound I in 30 ml glacial acetic acid is treated with 4 ml of a 2% solution of nitric acid in glacial acetic acid and the reaction mass kept at room temperature for 24 h. The mixture is then poured on 200 ml water; the precipitate formed is filtered off, washed with water to a neutral reaction of the wash waters, and dried in air. Yield 0.19 g of a mixture of nitrocompounds IV and VII, and unreacted porphyrazine I. The mixture is dissolved in 20 ml chloroform and chromatographed on silica gel; eluting first with hexane then with hexane-benzene, 1:1 gives 11 mg (6.5%) of compound VII, R_f 0.86 (hexane–benzene 1:2), mp 128-131°C. Besides this 35 mg (15%) of the dinitro compound IV and 0.14 g (70%) of compound I is obtained.

Cobalt Tetranitrotetra(tert-butyl)porphyrazine (VIII). A solution of 0.20 g (0.336 mmole) of the cobalt complex II [7] in 30 ml glacial acetic acid is treated with a mixture of 16 ml fuming nitric acid and 16 ml glacial acetic acid, precooled to 5-10°C; the mass is shaken for 3 min and poured on 500 ml water with ice. The technical product (0.35 g) is dissolved in benzene and chromatographed on silica gel with benzene as the eluent; 0.15 g of a substance with R_f 0.17 (benzene) is obtained with a small amount of a strongly polar substance. Repeated chromatography by consecutive elution with hexane and benzene gives 0.134 g (51.5%) of compound VIII, R_f 0.17 (benzene), mp > 360°C.

Cobalt Complexes of Nitro-Substituted Tetra(tert-butyl)porphyrazines (VIII, XI, XII). A mixture of 65 mg (0.103 mmole) of the dinitro-derivative IV, 65 mg (0.5 mmole) of anhydrous cobalt (II) chloride, and 1 mg ammonium molybdate in 8 ml trichlorobenzene is refluxed with stirring for 3 h until the complete disappearance of compound IV (as checked by TLC). The reaction mass is cooled and chromatographed on silica gel, eluting first with hexane until complete removal of trichlorobenzene and then consecutively with benzene–hexane 1:1 and benzene, separating the fraction with R_f 0.37 (benzene). Yield after removal of the solvent 14 mg (21%) of the cobalt complex of dinitroporphyrazine XI, mp 88-90°C.

In the same way 25 mg (0.037 mmole) of the trinitro-porphyrazine V gave by chromatography with a mixture of benzene–hexane 1:1 18 mg (67%) of the cobalt complex X, R_f 0.75 (benzene), mp 62-64°C.

In the same way 0.10 g (0.77 mmole) of the tetranitro compound VI and 0.10 g (0.77 mmole) of anhydrous cobalt (II) chloride in 30 ml trichorobenzene gave by chromatography of the reaction mixture with benzene–hexane 2:1 99 mg (92%) of compound VIII, R_f 0.17 (benzene), mp > 360°C. The compound is spectroscopically identical to the compound, obtained by nitration of compound II.

Zinc Complexes of Nitro-Substituted Tetra(tert-butyl)orphyrazines (XIII-XV). A mixture of 60 mg (0.095 mmole) of dinitroporphyrazine IV and 28 mg (0.128 mmole) of zinc acetate dihyrate in 10 ml trichlorobenzene is refluxed for 20 min and chromatographed on silica gel with chloroform. Yield 66 mg ($\sim$100%) of a mixture of zinc dinitroporphyrazines XIII with the nitrogroups in adjacent or opposity pyrrole fragments with R_f 0.31 (silufol, chloroform) (center of a poorly resolved "dubbell"). Mass spectrum, *m/e*: M(Zn^{64}) 690, M(Zn^{66}) 692, M(Zn^{68}) 694.

In the same way 50 mg of the trinitro-derivative V and 25 mg of zinc acetate in 15 ml trichlorobenzene, refluxed for 20 min and chromatographed on silical gel with chloroform, give 47 mg (86%) of complex XIV with R_f 0.17 (chloroform). In the same way the tetranitroporphyrazine VI gives with zinc acetate in 2-3 min the zinc complex XV with a yield of 100%.

Nitration of the Copper Tetra(tert-butyl)porphyrazine (III). A solution of 0.55 g (0.091 mmole) of the copper complex (III) in 100 ml acetic acid is treated at room temperature with a mixture of 45 ml fuming nitric acid and 45 ml glacial acetic acid. The mass is kept at this temperature for 2 h and poured on water; the precipitate is separated and chromatographed on silica gel with benzene–hexane, 2:1. The fractions separated are: 1) 91 mg (13.5%) of the trinitro-derivative IX, R_f 0.87 (silufol, benzene–hexane, 2:1). Mass spectrum, *m/z*: M(Cu^{63}) 734, M(Cu^{65}) 736; 2) 34.5 mg (45%) of the tetranitro-derivative X. R_f 0.39 (silufol, benzene–hexane, 2:1) Mass spectrum, m/z: M(Cu^{63}) 779, M(Cu^{65}) 781.

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