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SYNTHESIS OF NEW TETRAPHENYLPORPHYRIN MOLECULES CONTAINING HETEROATOMS OTHER THAN NITROGEN: II. TETRAPHENYL-21-SELENA-23-THIAPORPHYRIN AND TETRAPHENYL-21,23-DISELENAPORPHYRIN

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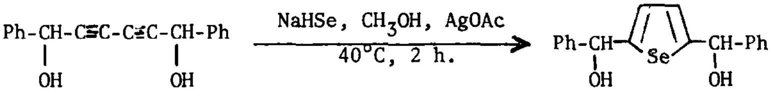
Earlier we described the introduction of heteroatoms other than nitrogen into the tetraphenylporphyrin skeleton for the case of the dithia analogue(1). The X-ray structure analysis of tetraphenyl-21,23-dithiaporphyrin(2) showed a very short distance between the two sulfur atoms (3.02 Å), which probably indicates an attractive interaction between these two atoms. Moreover, the geometry of the molecule, the distances between the meso-carbons, and other parameters seems to support this interaction. The large sulfur atoms ($r = 1.85$ Å)(3) are only 0.09 Å out of the NLS(4) plane, while the nitrogen atoms ($r = 1.5$ Å)(3) are 0.22 Å out of this plane.

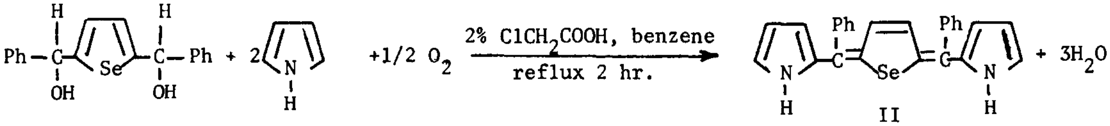
As the selenophene ring is not as aromatic as the thiophene one(5) and selenium is larger than sulfur ($r = 2.0$ Å)(3), it seemed to us that the syntheses of tetraphenyl-21-selena-23-thiaporphyrin (S,SeTPP) and tetraphenyl-21,23-diselenaporphyrin (Se_2TPP), might give important information bearing on the short S...S distance, as well as on the dependence of physical properties on the symmetry of the porphyrin skeleton.

Selenophenes were originally synthesized from acetylene and selenium at high temperature and pressure(6). A more general and convenient synthesis, starting from diacetylenes and NaHSe, was investigated by Curtis(7). We used, in principle, this way for the synthesis of the starting material:



I

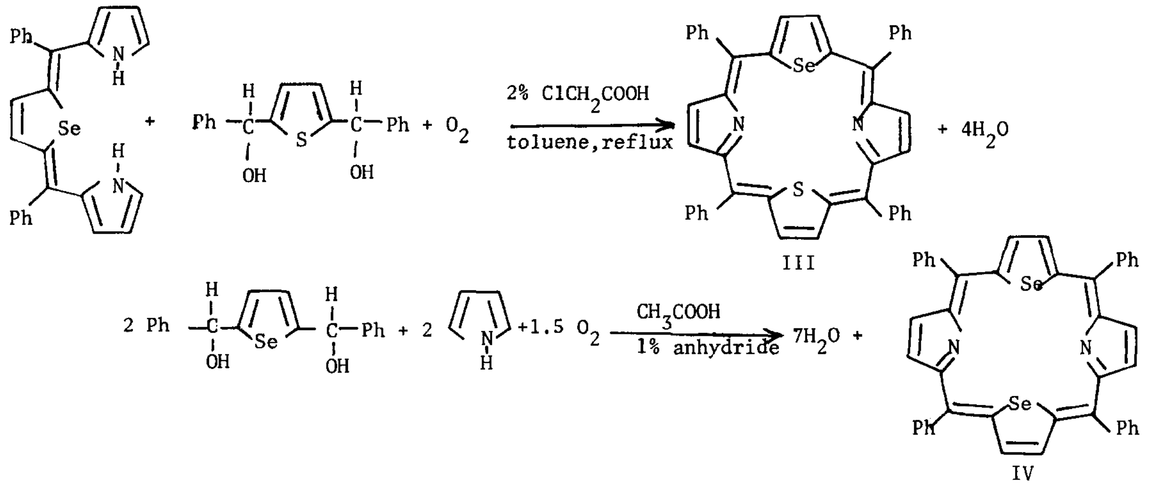
The reaction between I and an excess of pyrrole in acidic media gave the yellow 2,5-bis (α-phenylpyrrylmethylene) selenophene II in very good yield:



II

The reaction of II with 2,5-Bis (phenylhydroxymethyl) thiophene(1) in acidified toluene gave the expected tetraphenyl-21-selena-23-thiaporphyrin III.

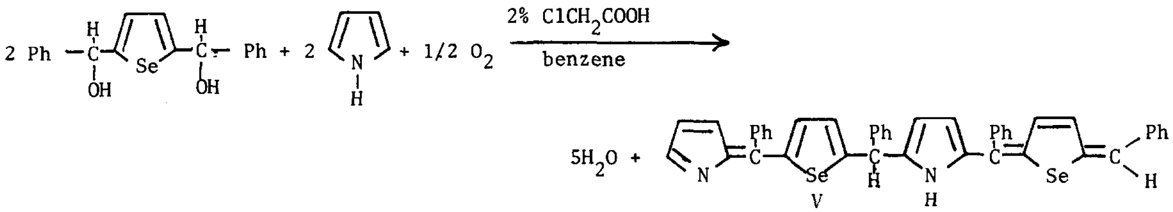
The reaction of dialcohol I with equivalent amount of pyrrole in acidic media gave tetraphenyl-21,23-diselenaphorphyrin IV:



III

IV

The reaction between I and equivalent amount of pyrrole is not as simple as that of the dithia analogue. When the reaction is carried out in benzene containing 2% (w/w) chloroacetic acid a yellow linear tetramer is formed. This is the 1-(phenylmethylene)-5,10,15-triphenyl-20,22-diselenabiladiene *ac* V :



V

This biladiene *ac* is an intermediate in the synthesis of the diselenaporphyrin, and when subject to the cyclization conditions, it yields the tetraphenyl-21,23-diselenaporphyrin. Table I shows the optical spectra.

TABLE I. Optical Spectra of Different Porphyrins.

	Soret, λ_{max},nm(ε)$^{(8)}$	bands, λ_{max}, nm (ε)$^{(8)}$			
		IV	III	II	I
Se$_2$TPP	447(185,000)	528(25,600)	-	632(2300)	694(3150)
S,SeTPP	441(233,100)	520(29,850)	551 (5070)	630(2550)	692(4300)
S$_2$TPP$^{(1)}$	435(297,500)	515(29,625)	548(7250)	632(2220)	699(4625)
TPP$^{(9)}$	419(464,000)	485(3800) 515(18,700)	548(8600)	592(5500)	647(3900)

Without going into details, subsequent substitution of NH by S and/or Se causes bathochromic shifts of the Soret bands, a gradual decrease of their extinction coefficients and a decrease of the extinction coefficient of the Q band III. These effect continue the trend reported for the previously discussed dithiaporphyrin.(1) The consistent decrease in absorption coefficient of the Soret band seems to indicate a decrease in aromaticity. In Table II the electronic spectra of the conjugate acids are given.

TABLE II. Optical Spectra of Different Porphyrin Conjugate Acids.

	Soret, λ_{max},nm(ε)(8)	Q bands λ_{max}, nm (ε)(8)	
		II	I
Se_2TPP (TFA)	469(199,000)	739(35,500)	760(40,750)
S,SeTPP (TFA)	466(250,000)	721(38,800)	756(37,750)
S_2TPP (TFA)(1)	456(335,000)	692(37,040)	739(33,030)
TPP (HCI)(10)	448(436,000)	608(9000)	659(50,900)

Simplification of the Q band structure occurs on protonation as before, and cannot be attributed to an increase of symmetry.(11) This simplification of spectra is found also for the metal complexes(1) and is probably connected with the introduction of charge into the π-system.

The X-ray structure analysis of Se_2TPP shows that the distance between the two selenium atoms is very short (2.85 Å) and that the selenium atoms are in the NLS plane.

EXPERIMENTAL

NMR spectra were determined with a Bruker 90 MHz spectrometer using tetramethylsilane as internal reference. Optical spectra were determined with a Cary 14 Spectrophotometer. Mass spectra were obtained by direct insertion into the ion source of a high reolution Varian MAT 731 mass spectrometer. Satisfactory C, H, N, S, Se analytical data were obtained for all new compounds.

2,5-Bis (phenylhydroxymethyl) selenophene (I). Liquid ammonia (750 ml) was distilled from sodium into a flask cooled in a solid carbon dioxide-isopropanol bath at -65°C. Sodium (9.2 gr) was added in portions under argon with stirring, and subsequently selenium (metal powder), was added slowly, in small portions, under argon, with stirring, until a very pale blue colour was obtained. The ammonia was evaporated off under argon. The white sodium selenide was heated under argon, on a water bath (50°C) to remove any residual ammonia. The flask was cooled in a salt-ice bath at -5°C and dry deairated methanol (750 ml) was added. The solution was stirred under argon for 30 min., and silver acetate (100 mg) was added. The stirring was continued for an additional 5 min. and 1,6-diphenyl-hexa-2,4-diyne-1,6-diol(12) (26.6 g, 0.1 mole) in dry deairated methanol (200 ml) was added dropwise, with stirring, for about 45 min. The mixture was warmed on a water bath at 40°C for 2 h., and left overnight. Water (1.L.) was added and the product was extracted with 1:1 ether-benzene (3x500 ml.). The organic layers were combined, washed with water (3x500 ml), saturated NaCl solution (500 ml) and dried over Na_2SO_4. Evaporation of solvents and crystallization from toluene gave 7.2 gr (21%) of white crystals, (diastereoisomer mixture). m.p. 136-137°C (decomposition).

nmr: δ 1.47 ppm (s); 2.25 ppm (s), 2.31 ppm (s), (2H); δ 4.26 ppm (d), J = 7 cps, (1H);
δ 5.76 ppm (d), J = 7 cps (1H); 7.35 ppm (m), (13H)

2,5-Bis (α-phenylpyrrylmethylene) selenophene (II). 2,5-Bis (phenylhydroxymethyl)selenophene (1.72 gr, 5x10^{-3} mole) and pyrrole (1 gr.) were refluxed (1 hr) in 500 ml of dry benzene (2% w/w chloroacetic acid). Chromatography on a dry acid-washed alumina (1 kg.) with benzene as eluent, gave orange solution. Evaporation gave 2.11 gr. (95%). As the material is air sensitive, a m.s. was taken and the next reaction was performed immediately.

m.s.: m/e 440 (M^+) (for ^{80}Se), $C_{26}H_{20}N_2Se$.

Tetraphenyl-21-selena-23-thiaporphyrin (III). 2,5-Bis (α-phenylpyrrylmethylene) selenophene (2.11 gr., 4.76x10^{-3} mole) and 2,5-Bis (phenylhydroxymethyl)thiophene, (1.41 gr) were refluxed (1.5 hr.) in toluene (1 L, 2% w/w chloroacetic). The solution was washed with 5% ammonia (2 x 500 ml), water (500 ml) and dried over $MgSO_4$. Evaporation of solvents, chromatography on basic alumina with 1:1 chloroform-benzene as eluent, followed by crystallization in a dessicator containing pentane, from a concentrated chloroform solution, gave 165 mg (10% yield) of red violet crystals.

n.m.r. δ 7.80 ppm (M)m (12H); 8.28 ppm (m), (8H); 8.73 (s), (4H); 9.58 (s), (2H);
δ 9.96 ppm (s) (2H); m.s.: m/e 690 (M^+) (for ^{80}Se), ($C_{44}H_{28}N_2SSe$).

Tetraphenyl-21, 23-diselenaporphyrin (II). 2,5-Bis (phenylhydroxymethyl) selenophene (3.43 gr, 10^{-2} mole) and pyrrole (700 mg) were refluxed in glacial acetic acid (1.5hr.,500ml 1% v/v acetic anhydride). The solution was diluted with cold water (1 liter), and extracted with chloroform (3x250 ml). The chloroform was washed with water (3x750 ml), ammonia solution (5%, 3x500 ml), water (500 ml) and dried over anhydrous $MgSO_4$. Evaporation and chromatography on basic alumina with 1:1 chloroform-benzene as the eluent, followed by crystallization from CH_2Cl_2, methanol (9:1) gave 760 mg (6%) of red violet crystals.

n.m.r.: 7.80 (m), 12H), 8.27 (m), (8H); 8.80 (s), (4H); 9.86 (s) (4H);
m.s.: m/e 744 (for ^{80}Se), ($C_{44}H_{28}N_2Se_2$).

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