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SYNTHESIS OF NEW TETRAPHENYLPORPHYRIN MOLECULES CONTAINING HETEROATOMS OTHER THAN NITROGEN. III. TETRAPHENYL-21-TELLURA-23-THIAPORPHYRIN: AN INTERNALLY-BRIDGED PORPHYRIN

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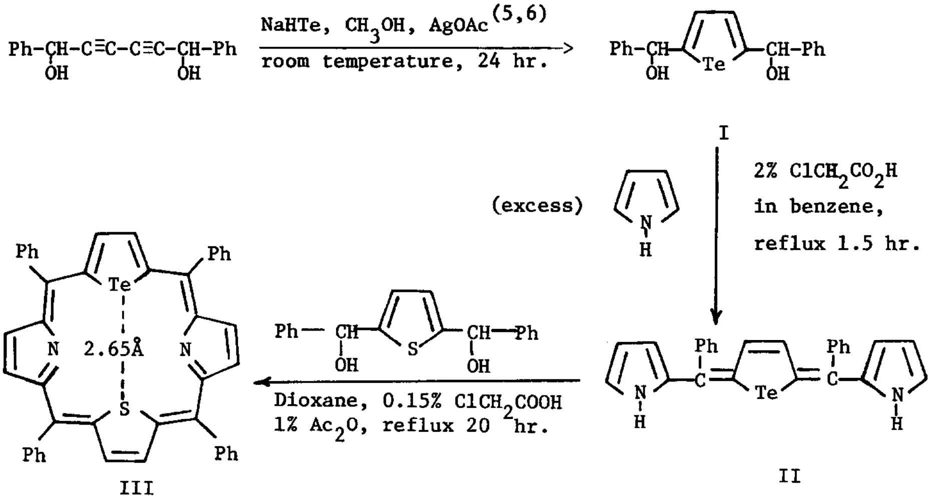
X-ray structure analyses of previously described tetraphenylporphyrin 'heterologs'(1,2) showed a gradual development of unusually short distances between the new heteroatoms in the porphyrin skeleton. Thus the distance of 3.02 Å for the S...S, 2.89 Å for S...Se and 2.85 Å for Se...Se(3), together with other molecular parameters does indicate the formation of a new chemical bond in these porphyrins.

Here we describe the synthesis of the title compound, where the S...Te distance (2.65 Å) is of the same order as S-Te bonds found in other compounds(4).

The same synthetic strategy as described for S,SeTPP(2) was followed:



The key for the above synthesis is a high boiling polar aprotic solvent and <u>catalytic</u> amounts of strong acid. Table I shows the optical spectra.

TABLE I: Optical spectra of different heterosubstituted tetraphenylporphyrins.

	Soret	Q-bands, λ_{max}, nm(ε)(7)			
	λ_{max}, nm(ε)(7)	IV	III	II	I
S,TeTPP(8)	445(90,900)	508*(12,630)	543*(7400)	625(3280)	668(2795)
Se_2TPP(2)	447(185,000)	528 (25,600)	-	632(2300)	694(3150)
S,SeTPP(2)	441(233,100)	520(29,850)	551*(5070)	630(255)	692(4300)
S_2TPP(1)	435(297,500)	515(29,625)	548(7250)	635(2220)	699(4625)
TPP(9)	419(464,000)	485(3,800) 515(18,700)	548(8600)	592(5500)	647(3900)

*Appears as a shoulder.

In all the heterosubstituted TPP molecules investigated, not only abnormally short distances are found between the new heteroatoms, but also between these heteroatoms and the nitrogens. In accordance with a recently proposed theory(10), we assume that the non-bonded electrons of the pyrrolenine nitrogens are also involved in bonding interactions within the core of the porphyrin. These interactions are crucial for the stability of the molecule and even traces of CF_3CO_2H which protonate the nitrogens are sufficient to decompose the molecule.

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 resolution Varian MAT 731 mass spectrometer. Satisfactory C, H, N, S, Te analytical data were obtained for the new compounds.

2,5-Bis(phenylhydroxymethyl)tellurophene (I) was synthesized(2) from NaHTe 1,6-diphenyl-hexa-2, 4-diyne-1,6 diol(11) in 52% yield. Crystallization from toluene, white crystals, m.p. 172°C. N.M.R. (DMSO-D) δ 1.47 ppm (s), 2.25 (s), 2.31 (s), (2H). δ 4.26 (d) J=7 Hz, (1H); δ 5.76 (d), J=7 Hz (1H); δ 7.35 (m), (12H).

2,5-Bis(α-phenylpyrrylmethylene)tellurophene (II) was synthesized from 2,5-Bis(phenylhydroxymethyl)tellurophene and pyrrole(2) in 73% yield.

m.s. m/e 487 (M^+, for ^{127}Te), $C_{26}H_{20}N_2Te$.

Tetraphenyl-21-telura-23-thiaporphyrin (III). 2,5-Bis(α-phenylpyrrylmethylene)tellurophenene (2.47 gr, $5x10^{-3}$mol) and 2,5-bis(phenylhydroxymethyl)thiophene (1.48 gr) were dissolved in dioxane (500 ml, dry distilled) containing chloroacetic acid (0.2%, W/W) and acetic anhydride (0.1% V/V). The mixture was refluxed for 20 h. After cooling the solution was diluted with water (1ℓ) and extracted with chloroform (3x250 ml). The chloroform was washed with water (3x750 ml), ammonia solution (5%, 250 ml), water (250 ml) and dried over $MgSO_4$. Evaporation and chromatography on alumina (basic) with benzene : chloroform 1:1 as the eluent followed by crystallization in a dessicator containing pentane, from a concentrated chloroform solution gave 2.44 mg (0.067%). M.s.: m/e 743 (M^+ for ^{127}Te), $C_{44}H_{28}N_2STe$. N.M.R.: δ 7.77 (m), (12H); δ8.23 (m), (8H); δ 8.71 (AB system, J_{AB}=4.7 Hz, Δν =7.3 Hz), (4H); δ 9.05 (s), (2H); δ 10.14 (s), (2H).

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