A Direct Link between Annulene and Porphyrin Chemistry—21-Vacataporphyrin

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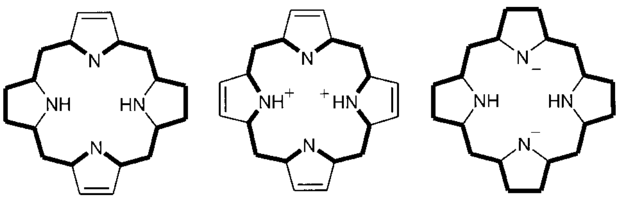
Abstract: A novel molecule, aza-deficient porphyrin 5,10,15,20-tetraaryl-21-vacataporphyrin has been synthesised by a substraction of a tellurium atom from 5,10,15,20-tetraaryl-21-telluraporphyrin under treatment of HCl. The new macrocycle is an annulene–porphyrin hybrid and at the same time is directly related to 21-heteroporphyrins but has a vacant space instead of heteroatomic bridge. The molecule preserves the fundamental structural and spectroscopic features of the parental 5,10,15,20-tetraarylporphyrin with three nitrogen atoms and two CH groups favorably prearranged for coordination.

Keywords: annulenes · porphyrinoids · tellurium

Introduction

A porphyrin macrocycle can be considered as a bridged diaza[18]annulene (**1a**, Scheme 1) with two isolated double bonds or as a tetraaza[16]annulene dianion **1b** with four -C_2H_2- bridges containing isolated double bonds.[1–3] Alternatively porphyrins can be formally derived from [20]annulene **1c** via the $C_{20}H_{20}^{2+}$ dication by introduction of the neutral bivalent NH and the negatively charged -N- links.[4, 5]



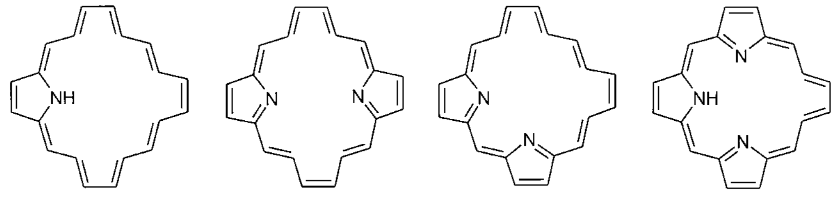
1a **1b** **1c**

Scheme 1. Annulenes imprinted into porphyrin.

The fact that a porphyrin contains an imprint of an annulene structure has been significantly stimulating in the construction of new porphyrinoids.[1, 6, 7] The [18]- or [16]annulene motives of geometry different then shown in Scheme 1, provided structural frames which led to discovery of new porphyrin related molecules, including heteroporphyrins, isomers of porphyrin (heteroporphyrins)—porphycene (heteroporphycene).[8–11] Construction of vinylogous porphyrins[12] and vinylogous heteroporphyrins[13] or in more general terms expanded porphyrins[11, 14] offers representative examples of inspiration by annulene chemistry.

For instance a stepwise porphyrin ring construction from [20]annulene can formally be carried out by introducing N and/or NH bridges. Such a route involves four different azabridged annulene structures represented here by **2**, **3**,[5, 15] **4** and **5** (Scheme 2). Evidently these molecules are located along the crossroad of porphyrin and annulene chemistry.

Three of them (**3**–**5**) are expected to demonstrate the aromatic nature by virtue of a built in $4n+2$ electron π-delocalization pathway (Scheme 2). Until present these hypothetical hybrids of porphyrin and annulene escaped any experimental investigations. Only the widely explored texaphyrin[16] **6a** (nitrogen-bridged expanded porphyrin—related to theoretically investigated secophyrin **6b**,[5] Scheme 3)



2 **3** **4** **5**

Scheme 2. Partially bridged annulenes—crossroad between porphyrins and annulenes.

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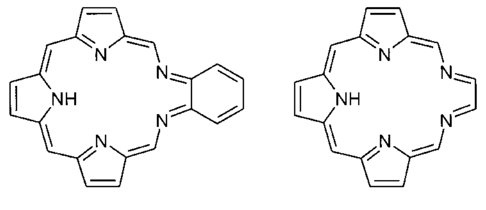


6a **6b**

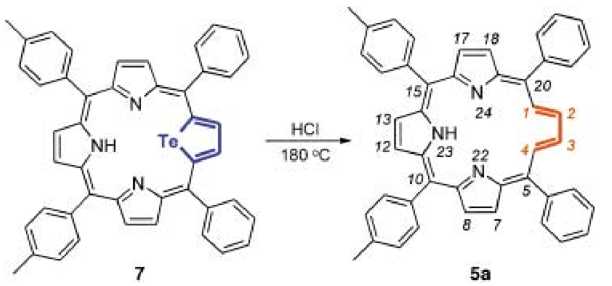
Scheme 3. Texaphyrin and secophyrin.

demonstrates a structural analogy to **5** provided two CH groups of **5** have been replaced by two nitrogen atoms.

In fact syntheses of **2**–**5** seem to be quite challenging when considering a rational approach by assembling all appropriate synthons. Enlightening for this chemistry is a "reversed" approach, which can be defined as the porphyrin chemists' view of annulenes.[1a] Namely, **2**–**5** can be considered as aza-deficient porphyrins which can be formed from **1** merely by extrusion of NH (N) bridging group(s) followed by addition of two hydrogen atoms. Thus a porphyrin (heteroporphyrin) molecule can be considered as a suitable substrate to form heterobridged annulenes. This kind of modification, introduced to 5,10,15,20-tetraarylporphyrin, produces a novel porphyrin-like molecule, namely 5,20-diphenyl-10,15-di(*p*-tolyl)-21-vacataporphyrin, (vac-dPdTP)H, **5a**, reported herein.[17, 18]

Results and Discussion

The synthetic work is summarized in Scheme 4. 5,20-Diphenyl-10,15-di(*p*-tolyl)-21-telluraporphyrin **7** has been used as a porphyrin-like substrate.[19] The choice of **7** has been motivated by the fact that this molecule, with a typical porphyrin structure, undergoes an intramolecular oxidative transformation into 21-oxaporphyrin. During this reaction the rigid porphyrin-like frame does not change. Thus, the fragile nature of the C-Te-C fragment makes **7** a good candidate to generate **5a**. Actually a straightforward conversion of **7** to **5a** requires an addition of hydrochloric acid at high-temperature conditions controlled by the solvent reflux temperature (1,2-dichlorobenzene). The reaction was stopped (1 h) once the brown-red solution of **7** turned peach-red. After chromatographic workup the product **5a** has been obtained in 55% yield.

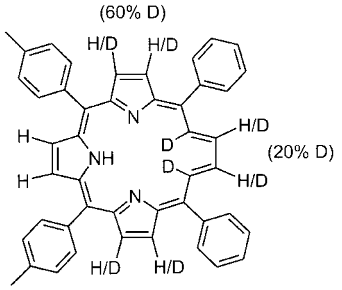


7 **5a**

Scheme 4. Synthesis of vacataporphyrin.

Abstract in Polish: *Otrzymano nowy typ molekuły—porfirynę pozbawioną jednego atomu azotu—5,10,15,20-tetraarylo-21-wakataporfirynę. Związek ten otrzymano przez eliminację atomu telluru z 5,10,15,20-tetraarylo-21-telluraporfiryny w wyniku reakcji z HCl. Nowy makrocykl jest hybrydą porfiryny i annulenu. Może być również traktowany jako 21-heteroporfiryna, w której w miejscu heteroatomu znajduje się luka. Molekuła zachowuje podstawowe właściwości spektroskopowe i strukturalne macierzystej 5,10,15,20-tetraaryloporfiryny i dysponuje trzema atomami azotu i dwiema grupami CH dogodnie ustawionymi dla koordynacji.*

The replacement of HCl by DCl yields a deuterated derivative **5b** where the deuterium atoms are bound to C1 and C4 (formerly α-tellurophene carbon atoms). This suggests that the reaction mechanism involves an electrophilic attack of $H^+(D^+)$ at these particular positions. The accompanying replacement of β-H atoms by deuterium as shown in Scheme 5 results from their acidic nature although disclosed under rather extreme conditions.



5b

Scheme 5. Deuterated vacataporphyrin.

Vacataporphyrin has been characterized by X-ray crystallography. The macrocyclic ring is nearly planar resembling the parent molecule **7**. The geometry is apparent form the views of the macrocycle in the Figure 1.

The electronic spectra of **5a** and its dicationic form $(\mathbf{5a}\text{-}H_2)^{2+}$ demonstrate the Soret-like bands accompanied by a set of Q-bands accounted for by aromatic nature of the compound (Figure 2).

The planar structure of solid **5a** is preserved in the solution as determined by ^{1}H NMR (Figure 3). The AA′XX′ pattern of H1, H2, H3, and H4 resonances is located in downfield and upfield regions of the spectrum (Figure 3) at $\delta_{1,4} = -2.50$, $\delta_{2,3} = 9.65$. These shifts are consistent with the aromatic structure accepting a ring current effect as a criterion. Actually the AA′XX′ multiplets serve as the fingerprint of the strictly annulene-like moiety (C1-C2-C3-C4). Remarkably, the NMR parameters of this pattern match those of [18]annulene.[20, 21] On the other hand ^{1}H NMR spectrum of the pyrrolic part of **5a** exhibits typical for tetraaryl-21-heteroporphyrins values of J and δ.

The labile proton is located on the central N23 nitrogen atoms and gives a broad singlet at 0.01 ppm; this demonstrates scalar coupling to H12 (CD_2Cl_2, 200 K). The ^{13}C chemical shifts of C1 (125 ppm) and C2 (132 ppm) are typical for sp^2

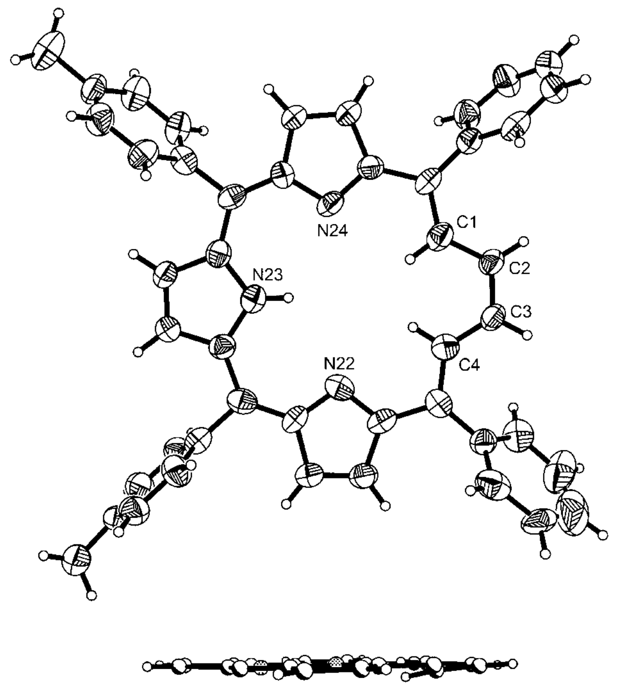


Figure 1. The crystal structure of **5a** (top: perspective view, vibrational ellipsoids represent 25% probability; bottom: side view, phenyl groups omitted for clarity).

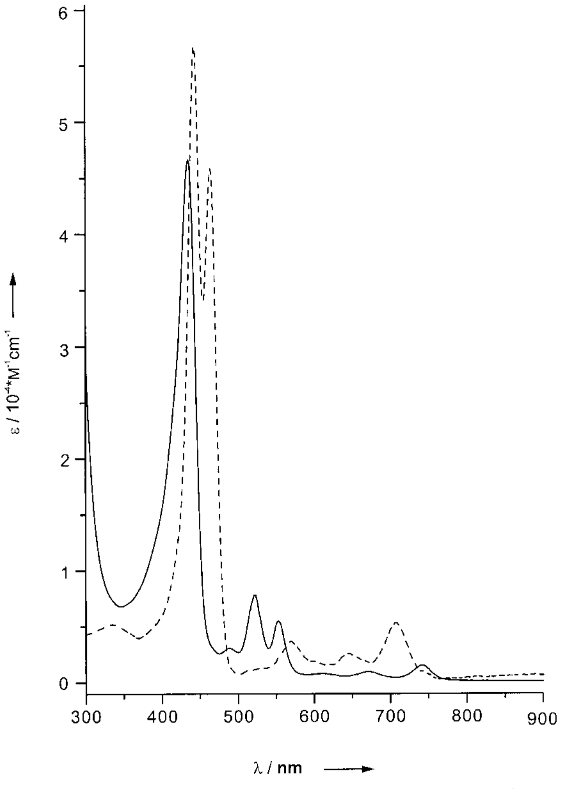


Figure 2. The electronic spectra of **5a** (solid line) and $(\mathbf{5a}\text{-}H_2)^{2+}$ (dashed line) in dichloromethane.

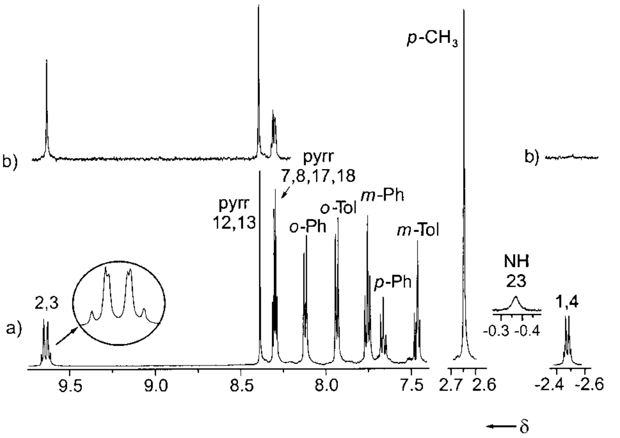


Figure 3. ^1H NMR spectrum of **5a** in [D]chloroform (selected downfield and upfield regions presented): a) 298 K; 23-NH in 220 K; b) **5b** obtained with DCl, selected regions; labeling follows the systematic position numbering of the porphyrin ring or denote proton groups: *ortho*, *meta* and *para* positions of *meso*-phenyl (Ph) or *meso-p*-tolyl.

carbon atoms built into aromatic–porphyrin or annulene rings.

Titration of **5a** with TFA results in formation of $(\mathbf{5a}\text{-}H_2)^{2+}$ which preserves the structural features of the neutral form but exhibits a larger ring current effect at H1 (–3.76 ppm) and H2 (10.20 ppm) positions and smaller at NH positions (H22, H24 at 1.57 ppm, and H23 at 2.81 ppm in 230 K).

Conclusion

Concluding, an extrusion of a tellurium atom from telluraporphyrin provides a noteworthy route to generate a nitrogen deficient tetraarylporphyrin. Vacataporphyrin, which clearly belongs to the family of core-modified porphyrins and resembles the parent 5,10,15,20-tetraarylporphyrin, has interesting properties as a ligand, as shown in preliminary investigations. The molecule naturally exposes three nitrogen and two hydrogen atoms to a coordinated metal ion.

Experimental Section

Preparation and characterization

The synthesis of ***5a***: A solution of 5,20-diphenyl-10,15-di(*p*-tolyl)-21-telluraporphyrin (**7**; 10 mg 0.013 mmol)[19] in deoxygenated *ortho*-dichlorobenzene (10 mL) and 20% HCl (1 mL) was placed in a 50 mL flask equipped with a reflux condenser. The nitrogen was bubbled through the solution for 20 minutes. The reaction mixture was then heated under reflux for 1 h. The solvent was evaporated, the residue was extracted with CH_2Cl_2 and purified by chromatography on basic alumina column. The first, minor fraction eluted with CH_2Cl_2 was unreacted **7**, the second was the peach-red major product **5a**. The title compound was recrystallized from $CHCl_3$ with CH_3OH (4.5 mg, 55%). UV/Vis (CH_2Cl_2) for **5a**: λ_{max} ($\log\varepsilon$) = 433 (4.7), 489 (3.4), 522 (3.8), 554 (3.6), 611 (2.8), 672 (2.9), 742 nm (3.1); ^1H NMR (500 MHz, $CDCl_3$, 298 K) for **2**: $\delta = 9.65$ (AA′XX′, $^3J(H1,H2) = 14.1$ Hz, $^3J(H2,H3) = 8.2$ Hz, $^4J(H1,H3) = -1.6$ Hz, 2H; vac 2,3), 8.38 (s, 2H; pyrr 12,13), 8.31, 8.29 (AB, $^3J(H,H) = 4.5$ Hz, 4H; pyrr 7,8,17,18), 8.12 (d, $^3J(H,H) = 7.0$ Hz, 4H; *o*-Ph), 7.93 (d, $^3J(H,H) = 7.6$ Hz, 4H; *o*-Tol), 7.75 (t, 4H; *m*-Ph), 7.66 (t, 2H; *p*-Ph), 7.46 (d, $^3J(H,H) = 7.6$ Hz, 4H; *m*-Tol), 2.65 (s, 6H; *p*-Tol (CH_3)), 0.01 (vbrs, 1H; NH 23), –2.50 (AA′XX′, 2H; vac 1,4).

For $(\mathbf{5a}\text{-}H_2)^{2+}$: ^1H NMR (5 equiv TFA, 298 K): $\delta = 10.20$ (AA′XX′, 2H; vac 2,3), 8.63, 8.61 (AB, $^3J(H,H) = 4.6$ Hz, 4H; pyrr 7,8,17,18), 8.38 (d, $^3J(H,H) = 7.7$ Hz, 4H; *o*-Ph), 8.31 (d, $^3J(H,H) = 7.7$ Hz, 4H; *o*-Tol), 8.23 (s, 2H; pyrr 12,13), 7.92 (t, 4H; *m*-Ph), 7.84 (t, 2H; *p*-Ph), 7.74 (d, $^3J(H,H) = 7.7$ Hz, 4H; m-Tol), 2.75 (s, 6H; *p*-Tol (CH_3)), +2.02 (brs, 2H; NH 22,24), –3.76 (AA′XX′, 2H; vac 1,4); HR MS: *m*/*z*: calcd for $C_{46}H_{36}N_3$: 630.2904

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[M^++H]; found: 630.2881; elemental analysis calcd (%) for $C_{46}H_{35}N_3 \cdot 0.8\,CHCl_3$: C 77.86, H 4.89, N 5.70; found: C 77.85 H 4.79, N 5.78.

Structure analysis: The measurement was performed on Kuma KM4 diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.54180$ Å) equipped with the scintillation counter, $T = 293$ K, in $\omega - 2\theta$ scan mode, $2\theta_{max} = 110°$. Studied crystals were prepared by the slow diffusion of isooctane into a solution of **5a** in chloroform to yield dark purple crystals of $C_{46}H_{35}N_3$. Crystal dimensions $0.25 \times 0.25 \times 0.40$ mm^3, monoclinic, space group $P2_1/n$, $a = 20.008(7)$, $b = 8.715(2)$, $c = 20.773(6)$ Å, $\beta = 102.88(3)°$, $V = 3531(2)$ Å^3, $\rho_{calcd} = 1.185$ gcm^{-3}, $Z = 4$, total number of reflections collected: 8241, number of independent reflections: 4401, of which 4401 were included in the refinement of 444 parameters, $\mu = 0.530$ mm^{-1}. The structure was solved using direct methods with SHELXS-97 and refined against $|F^2|$ using SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany, 1997), final R_1/wR_2 indices (for $I \geq 2\sigma(I)$): 0.1043/0.2983, max/min residual electron density: $+0.854/-0.272$ eÅ^{-3}, H atoms were fixed in idealized positions using the riding model constraints. CCDC-182197 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336033, or deposit@ccdc.cam.ac.uk).

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