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21,23-Dithiaporphycene: the First Aromatic Sulfur-containing System with Porphycene Structure

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Dedicated to Prof. Dr. Emanuel Vogel, University of Cologne, on occasion of his 65 th birthday

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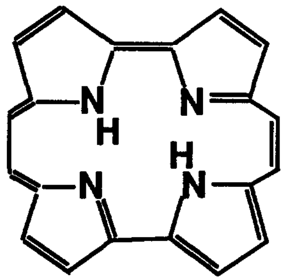
Abstract: A porphycene analogue where two nitrogen atoms have been replaced with sulfur has been prepared from 2-(2-thienyl)-*1H*-pyrrole. Its X-ray crystallographic data, UV/VIS and NMR spectroscopic properties proved the 18 π electrons aromaticity of the system, like porphycene.

Research work on porphyrines and related macrocycles has received in recent years considerable impulse from some advanced biomedical applications, such as fluorescent detection and photodynamic tumor therapy (PDT) [1] and virus inactivation [2], where the photosensitizer properties of these compounds are involved. A lot of experimental work [3] including *in vivo* tests [4] proves that the recently reported porphine isomer porphycene **1** and its alkyl derivatives [5] are very promising in this regard. Since a strong absorption at long wavelength is highly desirable, acetylene-cumulene or ethylene units were introduced into the structure of **1** which shows little absorption at about 700 nm to afford aromatic systems with λ_{max} as high as 889 nm, but only one of the prepared molecules is promising [3]. Moreover, it is known that the replacement of one [6] or two [7] pyrrole rings in a porphyrine with thiophenic units maintains the fully coniugated aromatic nature of the system causing a bathochromic shift of the low-intensity longest wavelength Q-band in the VIS-spectrum and that Q-bands are strong in **1**, therefore a sulfur containing porphycene-like molecule is expected to show a strong red-shifted absorption. On the other hand, thiophene units in macrocycles sometimes behave quite differently from pyrroles and furanes as shown by the 1,4: 7,10: 13,16-trioxido [18] annulene which is a true aromatic [18] annulene, whereas its sulfur analogue is best described as a cyclic triolephin where the thiophene rings maintain their own aromaticity [8].On these grounds, the synthesis of a sulfur-containing porphycene appeared interesting to us: so we report here the preparation and X-ray crystal structure of the 21, 23-dithiaporphycene **2**.



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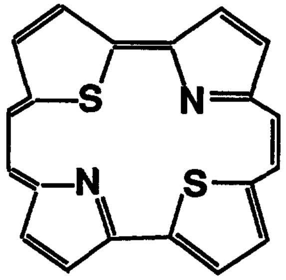
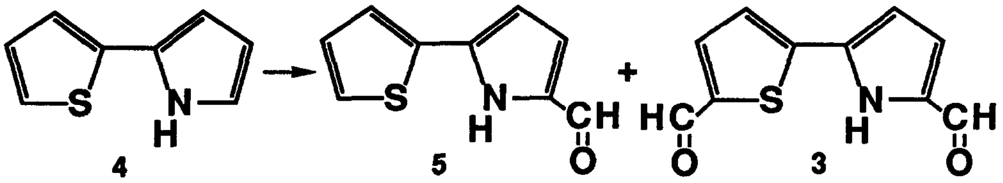


2

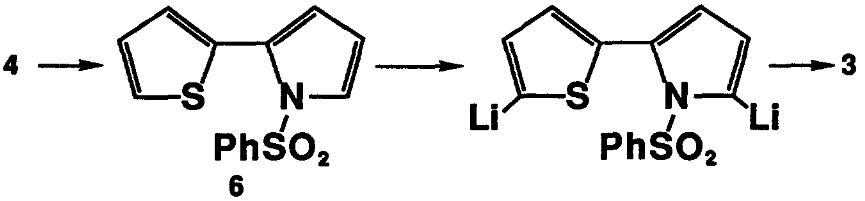
RESULTS AND DISCUSSION

The reductive dimerization through the McMurry reaction with low-valent titanium of dicarbonyl compounds is at present the only way to porphycenes and analogous systems although poor yields have always been reported [3, 5]; the dialdehyde 3 could be a very attractive precursor.The formylation of 2-(2-thienyl)-*1H*-pyrrole 4 [9] with an excess of Vilsmeier reagent in refluxing 1,2-dichloroethane was tried at first obtaining 5-(2-thienyl)-*1H*-2-pyrrolecarboxaldehyde 5 [10] (79.0%) together with very little 3 (2.1%) and suggesting a strong deactivation of the thiophene ring after the first electrophilic attack (Scheme n. 1).



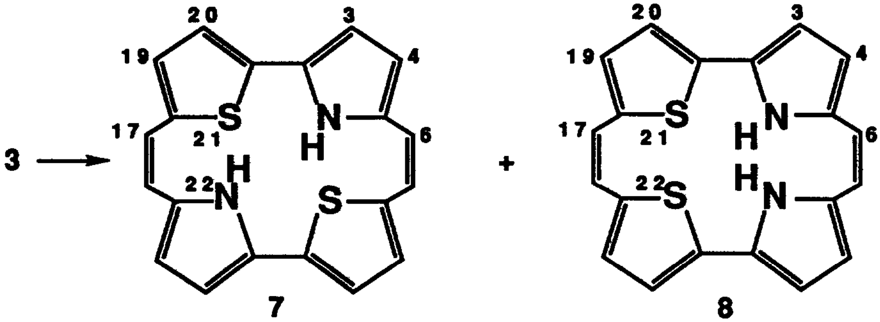
Scheme n. 1

As a high reactivity of N-phenylsulfonylpyrroles and indoles towards lithiating agents has been reported [11], a different way to 3 was then considered: the easily prepared 6 was reacted in THF with *t*-BuLi in a 1: 2.4 molar ratio followed by DMF; alkaline hydrolysis of the protecting group and chromatographic work-up gave 3 in 44.2% yield (Scheme n. 2).



Scheme n. 2

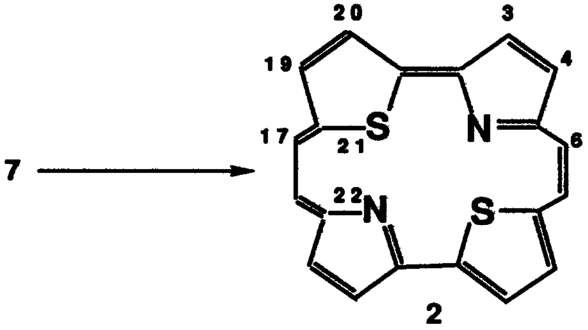
The performance of the McMurry reaction on 3 afforded 7, a dihydroderivative of 2, (8.1%) and 8 (0.4%) as bright-red and orange crystals respectively, together with much polymeric material (Scheme n. 3).



Scheme n. 3

7 and 8 resulted in air-stable crystalline compounds; this was somewhat unexpected, since during the synthesis of porphycenes [5] and tetraarylthia- or dithiaporphyrines [6, 7b, 7c] the final oxidation step to an aromatic system was readily performed by atmospheric oxygen. Air-stable porphyrinogens have been reported during the synthesis of highly substituted porphyrines [12] and their aromatization performed with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Analogously, when 7 in THF was treated with DDQ the formation of a bright violet colour took place and 2 was isolated in quantitative yield (Scheme n. 4)

2 is a stable, crystalline, violet, high-melting (> 300 °C) and sparingly soluble substance; a single crystal could be grown by evaporating very slowly a solution in THF/hexane (about 1/1) in the dark, thus allowing a X-ray structure determination whose relevant data are shown in Figure n.1. The molecular structure proposed for 2 in Scheme n. 4 is confirmed and its aromatic nature clearly proved. As a matter of fact, the normal bond length relation C_α-C_β < C_β-C_β for thiophene and pyrrole is reversed in 2 as observed in 1 [5a] and in the 21,23-dithia- and thiaporphyrine ring [7c] (mean values for 2 : C_α-C_β = 1.410 Å (thiophene), 1.438 Å (pyrrole), C_β-C_β= 1.375 Å (thiophene), 1.367 Å (pyrrole)) and, as in 1, the alternance of bond lengths in the olephinic bridges practically disappears. In addition, 2 is almost planar, as can be seen from the dihedral angles between



Scheme n.4

the five-membered rings and the middle plane of the olephinic carbon atoms, which are, following the numbering of the heteroatoms: 1.4° (2), 3.2° (1), 3.1° (1), 1.9° (1). A much larger deviation from planarity is observed in the 21,23-dithiaporphyrine system, where such deviations from the plane of the *meso* carbon atoms are: 4.9° (thiophene) and 12.9° (pyrrole) [7c] ; the planarity causes a notable distorsion of the olephinic CCC bonding angles in 2, which measure between 133.0° and 130.8°.

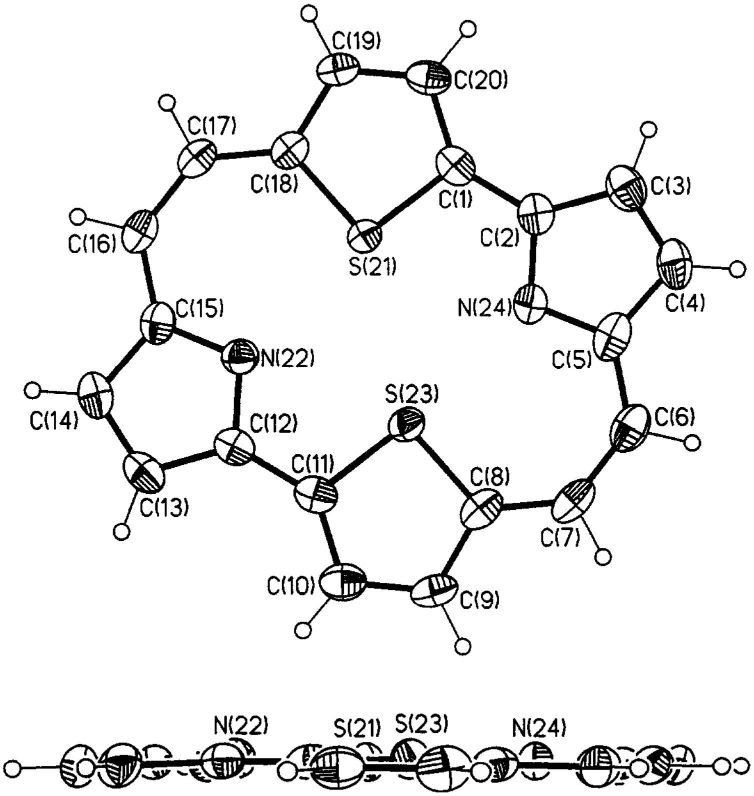


Figure n. 1. Crystal structure of 2: thermal ellipsoids (30% probability) and selected bond lengths (Å) and angles (°) with standard deviations in brackets. Top: top view, bottom: side view. C(1)-C(2) 1.426 (5), C(2)-C(3) 1.424 (5), C(3)-C(4) 1.357 (6), C(4)-C(5) 1.453 (6), C(5)-C(6) 1.410 (6), C(6)-C(7) 1.402 (7), C(7)-C(8) 1.407 (6), C(8)-C(9) 1.431 (6), C(9)-C(10) 1.384 (6), C(10)-C(11) 1.387 (6), C(11)-C(12) 1.430 (5), C(12)-C(13) 1.425 (5), C(13)-C(14) 1.377 (6), C(14)-C(15) 1.450 (6), C(15)-C(16) 1.406 (6), C(16)-C(17) 1.402 (6), C(17)-C(18) 1.410 (5), C(18)-C(19) 1.426 (5), C(19)-C(20) 1.366 (5), C(20)-C(1) 1.397 (6), C(5)-C(6)-C(7) 130.8 (4), C(6)-C(7)-C(8) 133.0 (4), C(15)-C(16)-C(17) 131.1 (3), C(16)-C(17)-C(18) 132.6 (3).

The distance between the nonbonded sulfur atoms (2.90 Å) is much shorter than the sum of the van der Waals radii (3.70 Å): a similar distance has been observed in the puckered 21, 23-dithiaporphyrine system [7c] (3.07 Å), but it has been shown that the S-S interaction does not play a role to estabilish the delocalization pathway within the macrocycle and a similar conclusion is perhaps valid also for **2**.

The characterisation of **2** could be completed through its NMR (^1H and ^{13}C), Mass and UV/VIS spectra. Table 1 shows ^1H-NMR data (300 MHz, $CDCl_3$) for compounds **2**, **7** and **8**. A slight concentration-dependence of δ-values (about 0.05 ppm) was observed for the first compound.To assign the ^1H-NMR spectrum of **2** it was assumed that its thiophenic protons show higher δ-values than the pyrrolic ones as observed in tetra(p-tolyl)thia-[6] and in tetraphenyl-21,23-dithiaporphyrine [7b] where protons on thiophene give singlets at δ= 9.78 and 9.68 respectively, whereas δ-values for pyrrolic protons range from δ= 8.92 to δ= 8.65; it must be noted that H(3) and H(4) in **2** are significantly shifted to higher fields than in **1** ($\delta_{H(3)}$= 9.67 and $\delta_{H(4)}$= 9.23 [5a])

Table 1. ^1H-NMR Data of **2**, **7**, **8**

	H(3)	H(4)	H(6)	H(17)	H(19)	H(20)
2	9.02 (dd) J_{34}= 4.3 Hz J_{320}= 0.4 Hz	8.79 (d) J_{43}= 4.3 Hz	9.55 (d) J_{67}=10.7 Hz	10.23 (d) J_{1617}= 10.7 Hz	9.78 (a) J_{1920}= 4.5 Hz	9.78 (a) J_{2019}= 4.5 Hz J_{203}= 0.4 Hz
7	6.23 (dd) J_{34}= 3.5 Hz J_{31}= 2.6 Hz	6.08 (dd) J_{43}= 3.5 Hz J_{41}= 2.8 Hz	6.27 (a) J_{67}= 11.6 Hz	6.27 (a) J_{1716}= 11.6 Hz J_{1719}= 0.7 Hz	6.84 (a) J_{1920}= 3.6 Hz J_{1917}=0.7 Hz	6.84 (a) J_{2019}= 3.6 Hz
8	6.22 (dd) J_{34}= 3.5 Hz J_{31}= 2.4 Hz	6.12 (dd) J_{43}= 3.5 Hz J_{41}= 2.8 Hz	6.00 (s)	6.62 (s)	6.92 (d) J_{1920}= 3.6 Hz	6.96 (d) J_{2019}= 3.6 Hz

(a) Tight AB-system showing further long-range coupling; δ_{NH} = 8.95 (**7**), 9.27 (**8**)

The decoupled ^{13}C-NMR spectrum of **2** (75.5 MHz, $CDCl_3$) shows ten signals at δ= 156.0, 154.4, 146.3, 145.4 (quaternary carbons), 139.7, 135.1, 127.6, 126.6, 124.2, 119.6; the low solubility of **2** did not allow a standard HETCOR experiment in a reasonable time, but a DEPTC experiment and the proton satellite spectrum provided one-bond carbon-hydrogen coupling constants whose comparison allowed an almost complete assignment for the protonated carbons. Pyrrolic carbons resonate at δ= 126.6 (C(3), $^1J_{CH}$= 172.8 Hz) and δ= 135.1 (C(4), $^1J_{CH}$= 171.5 Hz) whereas for porphycene $\delta_{C(3)}$= 125.8 and $\delta_{C(4)}$= 130.5 [5a] and for porphine δ= 131.5 [13] are reported, thiophenic ones at δ= 127.6 and δ= 139.7 ($^1J_{CH}$= 168.4 and 166.5 Hz, no more precise assignment was possible); the signals at δ= 124.2 (C(7), $^1J_{CH}$= 154.5 Hz) and δ= 119.6 (C(6), $^1J_{CH}$= 152.9 Hz) come from the olephinic carbons.

The mass spectrum of **2** (EI, 100 eV) shows the molecular peak as the basis peak with very little fragmentation; surprisingly, also pure samples of **2** show a M+2 peak stronger than what expected from the contribution of ^{34}S and whose intensity depends strongly from the operating conditions (among these, the type of metal of the sample crucible). A partial reduction of **2** clearly takes place, but other products (probably polymeric and nonvolatile) could not be identified.

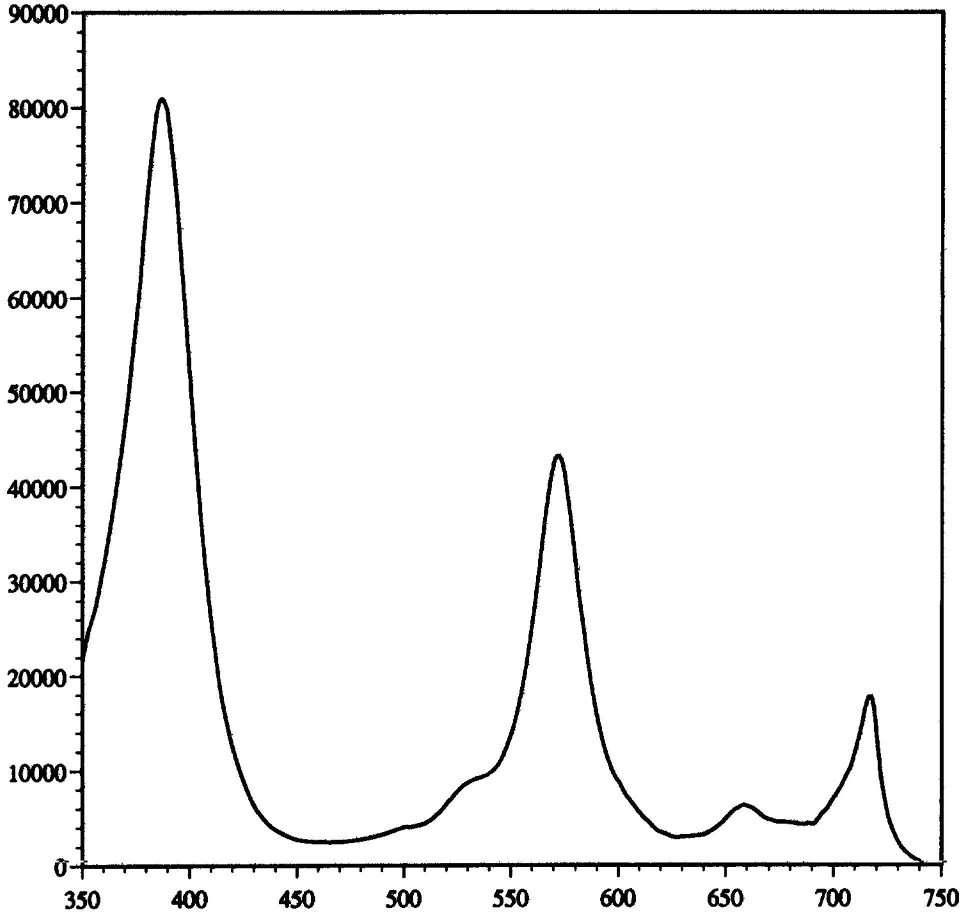


Figure n. 2. VIS spectrum of **2** in THF (ε / λ (nm))

The UV/VIS spectrum of **2** (THF) shows a strong absorption at 387 nm (ε= 81200) and several weaker bands at longer wavelengths (572 nm, ε= 43400; 661 nm, ε= 6100; 717 nm, ε= 17800). Whereas the first band can be considered as for porphyrines and porphycenes a typical Soret band, the long wavelength peak at

717 nm with an 87 nm bathochromic shift respect to porphycene confirms the prevision and **2** could be interesting for photodynamic tumor therapy applications. Moreover, an absorption maximum above 700 nm for tetrapyrrolic, 18π electrons macrocycles and their oxygen or sulfur analogues as free bases has been only very recently reported for a 23, 24-dioxa-5-oxophlorin [14].

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are uncorrected. ^{1}H-NMR spectra were run on AC-P 300 or AC-F 200 Bruker NMR instruments and standard COSY and NOE experiments used for spectral assignments. ^{13}C-NMR spectra were acquired at 75.5 MHz; the DEPTC experiment was performed with 3.6 sec. acquisition time and a digital resolution of 0.14 Hz/point reached with one zero-filling. UV/VIS spectra were measured on a CARY-118C instrument and mass spectra on a VARIAN MAT 311-A instrument at 100 eV. Petrol refers to 40-60 °C petroleum ether and peroxide-free THF was always used.

5-(2-Thienyl)-1H-2-pyrrolecarboxaldehyde (**5**) and *5-(5-formyl-2-thienyl)-1H-2-pyrrolecarboxaldehyde* (**3**)

To the Vilsmeier reagent from dry DMF (0.64 ml; 8.2 mmol) and phosphorus oxychloride (0.75 ml; 8.0 mmol) in dry 1,2-dichloroethane (10 ml), 2-(2-thienyl)-*1H*-pyrrole **4** (0.429 g; 3.0 mmol) in the same solvent (8 ml) was added. The mixture was magnetically stirred at room temperature for 90 min., at reflux for one hour, then cooled, added with sodium acetate saturated solution (15 ml) and stirred again at reflux for one hour. After cooling , the organic layer was separated, the aqueous one extracted with chloroform (10 ml), the combined and dried (Na_2SO_4) organic layers evaporated and the raw product purified through a flash chromatography (96.3 g silica gel in a 30 mm-wide column, eluent petrol / acetone= 3/1) to give **5** (0.420 g; 79.0% yield) m.p. 165-6 °C ($CHCl_3$ / hexane, Lit. 167-8 °C) and **3** (0.013 g; 2.1% yield), m.p. 232-4 °C (ethanol, after sublimation at 180 °C / 0.01 torr). ^{1}H-NMR (DMSO-d_6) (δ) 6.83 (d, J= 4.0 Hz, 1H; H(4)), 7.12 (d, J= 4.0 Hz, 1H; H(3)), 7.85 (d, J= 4.0 Hz, 1H; H(3')), 8.02 (d, J= 4.0 Hz, 1H; H(4')), 9.56 (s, 1H; pyrr. CHO), 9.91 (s, 1H; thioph. CHO), 12.82 (broad, 1H; NH). $C_{10}H_7NOS$ requires: C, 58.52; H, 3.44; N, 6.82. Found: C, 58.41; H, 3.42; N, 6.42.

1-Phenylsulfonyl-2-(2-thienyl)-1H-pyrrole (**6**)

A suspension of sodium hydride (from 0.751 g of 80% dispersion; 25.0 mmol) in dry DMF (10 ml) was added under nitrogen and magnetic stirring with a solution of **4** (3.050 g; 20.4 mmol) in dry DMF (10 ml) at 0 °C. The mixture was let to stir at room temperature for two hours then cooled again to 0 °C, added with benzenesulfonylchloride (3.2 ml; 25.1 mmol), stirred for 3 hours at room temperature, added with 20% sodium carbonate (20 ml) and extracted three times with ether (20 ml). The combined ethereal phases were washed four times with water, dried (Na_2SO_4) and evaporated. The residue was dissolved in 250 ml of benzene / hexane (1 / 1), filtered through a short silica gel plug to remove a coloured impurity and, after elimination of the solvent at reduced pressure, crystallized from ether / hexane at -50 °C to give **6** (3.540 g;

60.0%), m.p. 52-3 °C (ether / hexane). $C_{14}H_{11}NS_2O_2$ requires: C, 58.11; H, 3.83; N, 4.84. Found: C, 58.35; H, 3.76; N, 4.60.

Lithiation / formylation of **6**

To a solution of **6** (1.450 g; 5.0 mmol) in THF (22 ml) at -50 °C *t*-BuLi (1.82 M; 6.7 ml) was added under nitrogen; with magnetic stirring the mixture was let to reach -20 °C in 25 min. and added with dry DMF (1.20 ml; 15.5 mmol). The ensuing thick slurry was further stirred for 20 min. at -20 °C, 30 min. at room temperature and added with 5% Na_2CO_3 (5 ml). The organic phase was separated, the residue washed four times with THF (20 ml), the combined organic extracts (after removal of the solvent *in vacuo*) added with methanol (40 ml) and 2N NaOH (20 ml) and stirred at reflux under nitrogen for 4 h. After neutralization with glacial acetic acid, brine (100 ml) was added, the organic phase separated and the aqueous one extracted four times with THF (20 ml). The combined and dried (Na_2SO_4) organic phases were evaporated and the residue purified through a flash-chromatography (190 g silica gel in a 35 mm-wide column, eluent petrol / acetone= 3 /1) to give, after sublimation at 180 °C / 0.01 torr, **3** (0.455 g; 44.2%).

21,23-Dithia-22,24-diazapentacyclo [16. 2. 1. $1^{2,5}$. $1^{8,11}$. $1^{12,15}$] tetracosa-2,4,6,8,10,12,14,16,18, 20-decaene (**7**) and *21,22-dithia-23,24-diazapentacyclo [16. 2. 1. $1^{2,5}$. $1^{8,11}$. $1^{12,15}$] tetracosa-2,4,6,8,10, 12,14, 16, 18, 20-decaene* (**8**)

3 (0.426 g; 2.06 mmol) in THF (60 ml) was dropped slowly (140 min.) into the refluxing suspension of the McMurry reagent from titanium tetrachloride (2.15 ml; 19.6 mmol), activated zinc (2.600 g; 39.8 mmol) and pyridine (1 ml) in THF (85 ml) under nitrogen and magnetic stirring. Afterwards the mixture was stirred for 1 h at reflux, cooled to 0 °C and strongly basified with concentrated ammonia. The ensuing slurry was filtered, the filter cake washed with THF (100 ml), the combined and dried (Na_2SO_4) organic phases were evaporated and the residue purified through a flash-chromatography (34.6 g silica gel in a 20 mm-wide column, eluent petrol : acetone = 5/1) to give a mixture of **7** and **8** that was separated with the same eluent on PLC plates. **7**: 0.029 g (8.1%), m.p. 192-5 °C (benzene/cyclohexane). EIMS *m/z* (%) 346 (M^+, 100). $C_{20}H_{14}N_2S_2$ requires m= 346.0598, found 346.0599. **8**: 0.0014 g (0.4%), m.p. 187-91 °C (benzene/hexane). EIMS *m/z* (%) 346 (M^+, 100). $C_{20}H_{14}N_2S_2$ requires m= 346.0598, found 346.0599.

21,23-Dithia-22,24-diazapentacyclo[16. 2. 1. $1^{2,5}$. $1^{8,11}$. $1^{12,15}$]tetracosa-1,3,5(24),6,8,10,12(22),13, 15,17,19-undecaene (**2**)

7 (0.0116 g; 0.034 mmol) in THF (2 ml) at 0 °C was added with DDQ (0.0108 g; 0.048 mmol) in THF (1 ml). The violet mixture was let to stay 15 min. at room temperature, then purified through a flash-chromatography (25.0 g silica gel in a 20 mm-wide column, eluent THF / hexane = 2/1) to afford **2** in quantitative yield. M.p.> 300 °C (THF / hexane). EIMS *m/z* (%) 344 (M^+, 100). $C_{20}H_{12}N_2S_2$ requires: m= 344.0442, found 344.0442.

Crystal Data of **2**. $C_{20}H_{12}N_2S_2$, M= 344.4, monoclinic, a= 10.165 (4), b= 10.854 (4), c= 14.405 (4) Å, β= 100.30 (3)°, V= 1563.7 (9) $Å^3$, Dc= 1.463 gcm^{-3}, F(000)= 712, z= 4, λ= 0.71073 Å, μ= 3.28 cm^{-1}, spacegroup $P2_1/c$. A total of 3151 reflections were collected in the $3 \leq 2\theta \leq 50$ range by ω-2θ scan. 2762 of them were unique and, from these, 2005 were assumed as observed ($I > 2.5\sigma(I)$). Lorentz-polarization corrections were applied to the intensity data. The structures were solved by direct methods and subsequently completed by Fourier recycling. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms. A common thermal parameter was assigned to these atoms. The final R value was 0.051, R_w= 0.063, S= 1.06. The weighting scheme used in the last refinement cycles was $w^{-1} = [\sigma^2 (F_o) + 0.0050(F_o)^2]$. Solutions and refinements were performed with the SHELXTL PLUS system (SHELXTL PLUS, version 3.4, Siemens Analytical X-ray Instruments Inc., Madison Wisconsin, 1989). Positional parameters, molecular dimensions and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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