21,23-Dithia-3,13-diazaporphycenes − Novel Aromatic Porphycene Analogues Incorporating Thiazole

Thomas Nußbaumer,[a] Claus Krieger,[b] and Richard Neidlein*[a]

Dedicated to Prof. Dr. Dr. h.c. mult. Günther Wilke (MPI Mülheim/Ruhr) on the occasion of his 75th birthday

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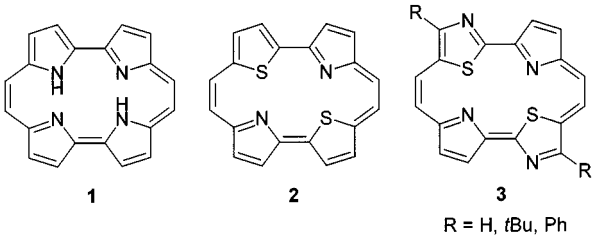
The syntheses of the first examples of aromatic thiazole-containing porphycene analogues **3** have been accomplished by oxidation of the corresponding 3,20:10,13-diepithio-6,9:16,19-diimino-1,11-diaza[20]annulenes **9** with DDQ. Compounds **9a–c** have been synthesized by McMurry coupling reaction of the diformylated 2-(1*H*-pyrrol-2-yl)thiazoles **8a–c**, readily available by a three-step reaction sequence using 2-pyrrolethiocarboxamide (**4**) as starting material. The aromaticity of the 21,23-dithia-3,13-diazaporphycenes **3** is clearly established by NMR and UV/Vis spectroscopy and verified by X-ray crystal structure analysis of **3b**.

Introduction

Structurally modified porphyrins, porphycenes, and related conjugated macrocycles are of particular interest due to their potential use as photosensitizers for biomedical applications such as fluorescence detection, photodynamic therapy (PDT) and viral inhibition.[1] Photodynamic therapy, a new technique for the treatment of diseased tissue, is based on the ability of such macrocycles to accumulate in malignant tissue;[1g,1h] when irradiated with laser light they can generate singlet oxygen, which destroys the cancerous cells.[1c−1h] The efficacy of this kind of therapy depends on the ability of the laser light to penetrate efficiently through human tissue, which increases strongly at wavelengths larger then 630 nm.[1c−1h] In this context, many attempts have been made to modify the porphyrin ring system to generate more effective chromophores for PDT, absorbing between 630 and 800 nm. Expanded, reshuffled, inverted, contracted, and otherwise modified porphyrin ring systems have been synthesized.[2] Strong absorption at long wavelengths is desirable, and so in previous publications we reported the syntheses of sulfur-containing porphycene analogues, namely tetraepithio[20]annulene and 21,23-dithiaporphycene (**2**) (Scheme 1), and observed remarkable changes in the structural and chemical properties of these compounds.[3]

Various groups have investigated the effects of replacing carbon atoms at the peripheral positions of porphyrins and porphyrin-like systems with nitrogen.[4] Such derivatives



Scheme 1

show bathochromic and hyperchromic shifts of the Q-band absorption relative to the parent compounds and are promising photosensitizers for PDT. However, the effects of introducing additional nitrogen atoms into porphycenes have not been studied. Compared to porphycene, compound **2** exhibits a strong bathochromic shift of 87 nm in the UV/Vis spectrum. Therefore, we became interested in the effect of additional nitrogen atoms in the β-position of the thiophene rings of **2** and so aimed at the syntheses of thiazole-containing[5] porphycene analogues **3** in order to combine the properties found in **2** and those found in nitrogen-containing, porphyrin-like macrocycles.

Results and Discussion

The intermolecular reductive coupling of dicarbonyl compounds with low-valent titanium under McMurry[6] conditions has become established as the most efficient method for the syntheses of porphycenes (**1**) and related macrocycles.[2c−2f,7] Thus, the diformylated substituted 2-(1*H*-pyrrol-2-yl)thiazoles **8a−c** should be suitable precursors in the preparation of **3a−c**. Compounds **8a−c** were readily available by a three-step reaction sequence using 2-pyrrolethiocarbamide (**4**)[8] as starting material. The key step in the syntheses of **8a−c** is the formation of the 1,3-thiazoles **6a−c** by cyclocondensation of **4** with correspond-

[a] Pharmazeutisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 364, 69120 Heidelberg, Germany
Fax: (internat.) + 49-(0)6221/546430
E-mail: richard.neidlein@urz.uni-heidelberg.de
[b] Max-Planck-Institut für Medizinische Forschung,
Jahnstraße 29, 69120 Heidelberg, Germany
Fax: (internat.) + 49-(0)6221/486219
E-mail: krieger@mixi.mpimf-heidelberg.mpg.de

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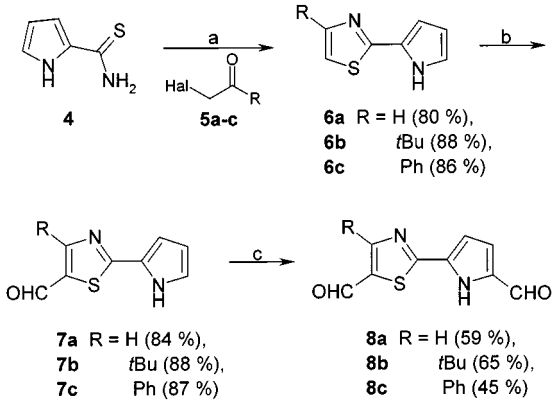
ing α-halo ketones **5a**−**c** (R = H, *t*Bu, Ph).[8a,9] Using this method, it was easily possible to introduce different substituents in the 4-position of the 1,3-thiazole ring, giving high yields of **6a**−**c** (Scheme 2).

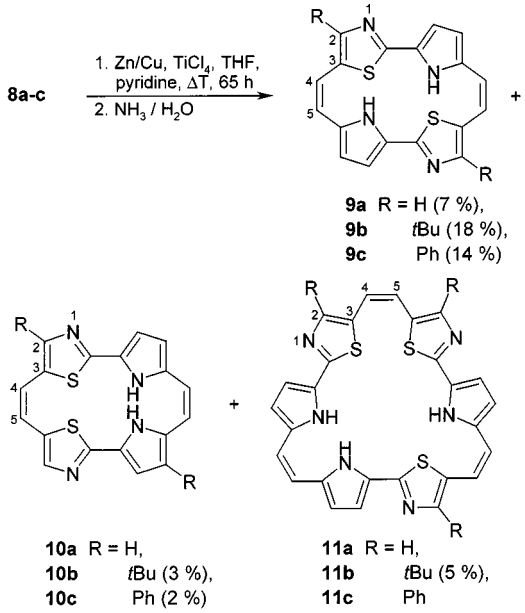


Scheme 2. Reagents and conditions: a) **5a**: R = H, X = Cl, toluene, Ac_2O, reflux, 60 min; **5b**: R = *t*Bu, X = Br, EtOH, reflux, 30 min; **5c**: R = Ph, X = Br, EtOH, reflux, 30 min; b) (i) 2 eq. *n*BuLi, THF, –78 °C, 60 min, (ii) *N*-FMP, –78 °C to –0 °C, 6 h, then H^+/H_2O; c) $POCl_3$/DMF, CH_2Cl_2, –10 °C to 20 °C, 3 h, tne NaOAc/H_2O

Because of the different reactivities of the 5-position of the 1,3-thiazole and the 5′-position of the pyrrole in **6a**−**c**,[9,10] we decided to synthesize **8** by a stepwise formylation of the 1,3-thiazole[11] and the pyrrole[8c] moieties (Scheme 2).

Thus, after treatment of **6a**−**c** with two equivalents of *n*-butyllithium in dry THF at −78 °C and quenching of the resulting 5-lithiated intermediates of **6** with *N*-formylmorpholine (*N*-FMP), the desired monoformylated products **7a**−**c** could be obtained in good yields (Scheme 2). In the case of the *tert*-butyl-substituted derivative **6b**, the reaction mixture had to be warmed up to −30 °C for 60 min after addition of *n*-butyllithium to complete deprotonation. Reaction of **7a**−**c** with Vilsmeier reagent ($POCl_3$/DMF) prepared in situ in dichloromethane furnished the diformylated 2-(1*H*-pyrrol-2-yl)thiazoles **8a**−**c** in satisfactory yields (Scheme 2).

According to literature procedures,[3,7] the reductive McMurry-type dimerisation of the diformylated subunit **8a** with low-valent titanium prepared by treatment of $TiCl_4$ with Zn/Cu couple in the presence of pyridine in THF gave, after workup with ammonia, the desired 3,20:10,13-diepithio-6,9:16,19-diimino-1,11-diaza[20]annulene (**9a**) in poor yields. The main product of the reaction was a yellow oil containing a mixture of 4,5-di- and 4,5,14,15-tetrahydrogenated derivatives of **9a**, which could not be separated by column chromatography.[3b][3c] Our experiments revealed that the observed hydrogenation was caused by reduction of the annulene with nascent hydrogen generated by the reaction of excess Zn/Cu couple with ammonia during the workup procedure. Therefore, removal of the reducing agent from the reaction mixture by filtration before the workup with ammonia yielded the desired 1,11-diaza[20]annulene **9a** together with considerable polymeric material. After chromatographic purification, **9a** was isolated as yellow, air- and light-stable crystals in a yield of 7%, which compares well with those of related conversions.[3,7] However, no formation of the theoretically possible compound **10a** (R = H) and of the trimer **11a** (R = H) could be observed (Scheme 3).



Scheme 3. McMurry coupling of diformylated precursors **8a**−**c**

This methodology was applied to dimerisation of the corresponding dicarbaldehydes **8b** and **8c**. In both cases, intermolecular McMurry coupling afforded after chromatographic purification three fractions containing the corresponding crude products **9**, **10**, and **11**. The yellow crystalline 1,11-diaza[20]annulenes **9b** and **9c** were obtained as the main products from the first fractions in 18 and 14% yield, respectively. Additionally, the isomeric *tert*-butyl- and phenyl-substituted 1,8-diaza[20]annulenes **10b** and **10c** were isolated as by-products from the second fractions in yields of 3 and 2%. The third products of the McMurry coupling were the 1,8,21-triaza[30]annulenes **11b** and **11c**, obtained as red microcrystalline powders of which only **11b** could be purified and characterised. Possible reasons for the higher yields of **9b** and **c** and the formation of **10b** and **c** and **11b** and **c** are the better solubility of the dicarbaldehydes **8b** and **8c** and the preorientation of the formyl group induced by the restriction on conformational freedom imposed by the bulky β-substituent.[12]

UV/Vis and NMR spectra of the obtained diaza[20]annulenes **9** and **10** do not show the typical behaviour expected for a 4*n*-π-annulene of planar molecule structure.[13] The ^{1}H-NMR spectrum of the parent compound **9a**, for example, shows an ABX system for the pyrrole protons at δ = 8.81 (NH), 6.65 (8,18-H) and 6.19 (7,17-H), one singlet for the thiazole protons at δ = 7.50 (2,12-H), and one singlet for the olefinic protons at δ = 6.48 (4,5,14,15-H);[14] indicative of a symmetrical structure without an obvious ring current.[3a,15] In the UV/Vis spectra of **9**, which show no absorption maximum over 400 nm, it can be seen that there

is only modest conjugation between the heterocyclic units as expected for a nonplanar conformation.[3,16] The spectroscopic properties of the 1,8-diaza[20]annulenes **10b**,**c** are very similar to those of **9a**−**c**. The cyclophane-type structure implied by these spectroscopic studies for the annulene skeleton of **9** and **10** is confirmed by the crystal structure of **9a** (Figure 1).

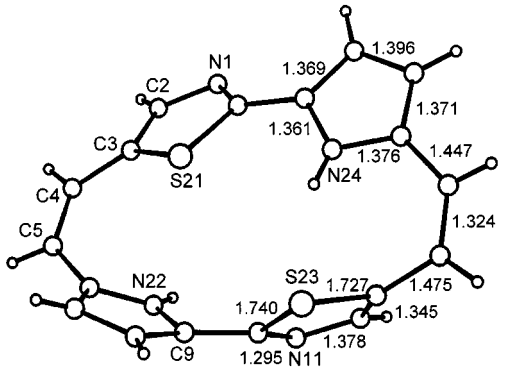


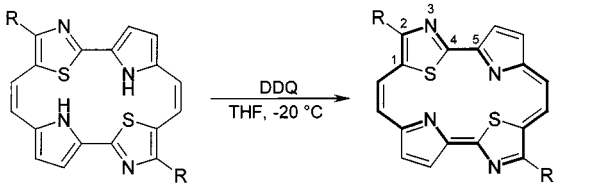
Figure 1. Molecular structure of cyclophane **9a** in top view; selected bond lengths [Å]

Compound **9a** has a nonplanar C_1-symmetrical conformation. It contains one pyrrole-thiazole subunit with synclinal, and one with anticlinal arrangement of the heterocycles. In both cases the pyrrole and thiazole rings are twisted. The synclinal pyrrole-thiazole subunit is located approximately perpendicular to the plane of the anticlinal pyrrole-thiazole subunit (Figure 1).

The ^{1}H-NMR spectrum of the triaza[30]annulene **11b** is very similar to that of **9b**, even though it is formally a $(4n + 2)$-π system while **9b** is a $4n$-π system. This and the absorption maxima in the UV/Vis spectrum of **11b** indicate that there is no obvious aromatic ring current in the molecule besides that of the heterocycles themselves and it can be assumed that the molecule is nonplanar.[16]

The aromatization of the air-stable dihydroporphycenes **9a**−**c** could be performed with several oxidation reagents, such as iodine, bromine or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[3a,15] Best results were obtained by treatment of solutions of **9** in THF with DDQ at −20 °C, which gave blue-green solutions, indicative of successful conversion. In attempts to isolate **3** by flash chromatography on silica or aluminium oxide, only decomposition of the product could be observed. However, **3a**−**c** could be successfully isolated without column chromatography after basic workup of the reaction mixture and recrystallisation of the crude product as violet crystals with a metallic lustre (Scheme 4). In the solid form, compounds **3a**−**c** are stable to air and light and could be stored for months under ambient conditions. However, solutions of **3a**−**c** are sensitive to acids.

The ^{1}H-NMR spectra of **3a**−**c** show for all ring protons a downfield shift induced by the diamagnetic ring current. For example, in the ^{1}H-NMR spectrum of **3a** one singlet is observed at δ = 10.32 (2,12-H), corresponding to the thiazole protons, together with four AB systems corresponding to the *meso*-protons [at δ = 9.95 (10,20-H) and 9.28



Scheme 4. Oxidation of **9a**−**c** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)

(9,19-H)] and the pyrrole protons [at δ = 8.87 (6,16-H) and 8.39 (7,17-H)]. The electronic spectra of **3** also indicate the aromatic character of these compounds. The UV/Vis spectra display an intense band at 375−410 nm, and several less intense absorptions at 680−780 nm (Figure 2). The first absorption (at 375−410 nm) is analogous to the typical Soret band of porphyrins and porphycenes, while the absorptions at longer wavelengths are similar to the Q-bands.[2][3a] The longest wavelength of the Q-band of **3a**−**c** shows a bathochromic shift of 110−146 nm with respect to porphycene and a shift of 23−59 nm in comparison with **2**. This confirms our prediction, and **3a**−**c** could be interesting for photodynamic tumour therapy (PDT).

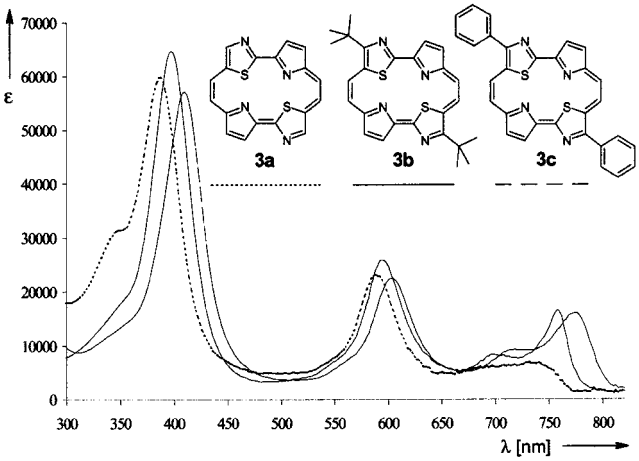


Figure 2. Electronic absorption spectra of 21,23-dithia-3,13-diazaporphycenes **3a**−**c** in THF ($c \approx 2 \times 10^{-5}$ mol/L)

In mass spectrometry, standard ionisation methods like EI or FAB gave exclusively the $[M^+ + 2]$ peak, as had already been observed for the related dithiaporphycene **2**.[3a] The molecular ions of **3a**−**c** were only observed by FD mass spectrometry. Finally, a single-crystal X-ray structure analysis demonstrated the planar aromatic character of **3b** as deduced from its spectroscopic properties.[17] Compound **3b** is a centrosymmetric molecule and has a nearly planar ring skeleton with a maximum deviation of ±0.07 Å of the carbon, nitrogen, and sulfur atoms from the least-square

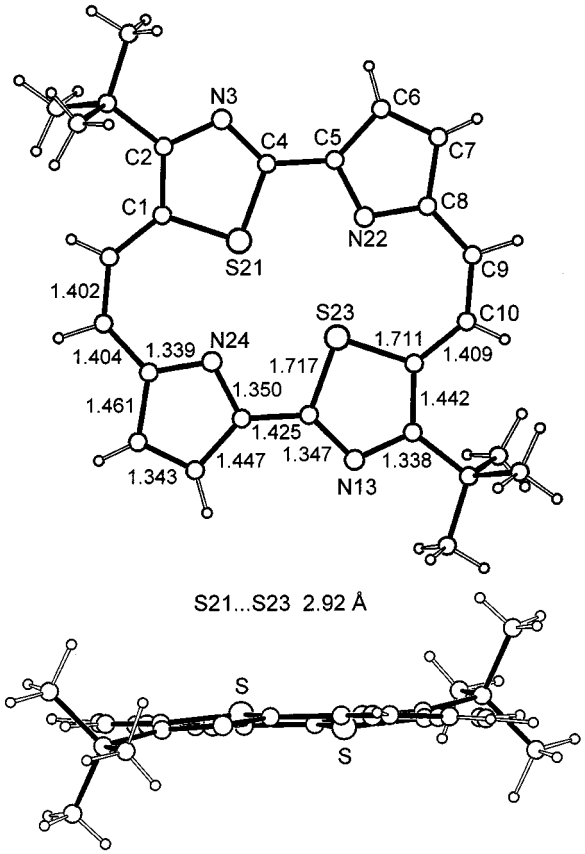


Figure 3. Molecular structure of **3b** in top view (top) and in side view (bottom); selected bond lengths and distances [Å]

plane (Figure 3). Compared with the 1,11-diaza[20]annulene **9a**, the alternation of the bond lengths in the olefinic bridges (C8−C9−C10−C11) practically disappears in **3b** and the normal bond-length relationship of $C_\alpha-C_\beta < C_\beta-C_\beta$ for thiazole and pyrrole is reversed in **3b**, as observed in porphyrins and porphycenes. The planarity causes a notable distortion of the C−C−C bonding angles of the *meso*-carbon atoms in **3b** of 133.2 and 132.1°. The distance of 2.92 Å between the nonbonded sulfur atoms (S21−S23) in **3b** is much shorter than the sum of the van der Waals radii for two sulfur atoms (3.70 Å),[18] but longer than that of a typical S−S single bond (2.08 Å).[17] It has been shown that the S−S interaction is very weak and does not play a role in determining the delocalisation pathway within such macrocycles.[19] Similar distances have been observed in **2**[3a] (2.90 Å) and in the 21,23-dithiaporphyrin system[20] (3.07 Å).

In further studies, we were interested in the oxidation of the 1,8-diaza[20]annulenes **10b** and **c**, to generate the corresponding 21,24-dithia-3,16-diazaporphycenes. However, several attempts to convert **10b** or **10c** into the desired 21,24-dithia-3,16-diazaporphycenes, by oxidation with different oxidation reagents, all failed. Only the fast decomposition of **10b** or **10c** could be observed. One possible explanation for this could be that the two sulfur atoms, because of their large size, cannot be accommodated within the core of the macrocycle to create a stable, planar π-conjugation system.

Conclusion

A series of thiazole-containing porphycenes **3** was prepared by oxidation of the 1,11-diaza[20]annulenes **9** with DDQ. The aromaticity of the compounds **3** was verified by NMR and UV/Vis spectroscopy and finally by X-ray crystal structure analysis of **3b**. The precursors **9** were easily obtained in modest yields by McMurry coupling of the dicarbaldehydes **8**; the formation of hydrogenated by-products could be explained. A convenient synthesis has been developed for compounds **8**, using 2-pyrrolethiocarboxamide (**4**) as starting material. The absorption spectra of **3a−c** show the postulated bathochromic shift (740−776 nm) of the long-wavelength absorption band and so they could be interesting compounds for PDT.

Experimental Section

General Remarks: All reactions requiring anhydrous and anaerobic conditions were carried out under argon in flame-dried glassware. Solvents were purified and dried according to standard procedures.[21] THF was distilled from potassium/benzophenone immediately prior to use. Silica gel (60−200 mesh) for column chromatography was obtained from Merck KGaA, Darmstadt. − Melting points were determined with a Reichert hotstage and are uncorrected. − UV/Vis spectra were recorded with a Hewlett Packard HP 8452A Diode Array spectrophotometer. − Infrared spectra were obtained as KBr pellets with a Perkin−Elmer PE 1600 FT-IR spectrophotometer. − ^{1}H-NMR spectra were recorded at 250 MHz with a Bruker WM-250 or at 360 MHz with a Bruker AM-360. ^{13}C-NMR spectra were measured at 62.9 MHz or at 90.6 MHz with the Bruker spectrometers described above; δ values are in ppm downfield from internal TMS. The degree of carbon substitution was determined by *J*-modulated spin-echo experiments. − Mass spectra were obtained with a Varian MAT-311 A mass spectrometer or JOEL JMS-700 sector field mass spectrometer. − Elemental analyses were performed with a Foss-Heraeus Vario EL.

X-ray Crystallographic Study: Crystals suitable for X-ray diffraction studies were obtained by slow recrystallization of **9a** from benzene and of **3b** from chloroform. Measurements were performed at room temperature with an Enraf−Nonius CAD4 four-circle diffractometer equipped with a graphite monochromator using Mo-K_α radiation (λ = 0.71073 Å) and an ω/2θ scan mode. The structures were solved by direct methods (SIR 98) and refined by full-matrix least squares on *F* with all measured unique reflections. Hydrogen atoms were located and refined isotropically. Table 1 summarizes details of the crystal data, the data collection, and the structure refinement. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-136931 (**9a**) and -136932 (**3b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

2-(1′*H*-Pyrrol-2′-yl)thiazole (6a): Chloroacetaldehyde (**5a**) (50% in water, 10 mL) was extracted with diethyl ether (12 mL), dried with $MgSO_4$, and filtered. This solution was added to a suspension of 2-pyrrolethiocarboxamide (**4**)[8] (2.52 g, 20.0 mmol) and acetic anhydride (2.50 mL, 22.5 mmol) in toluene (10 mL). The mixture was

Table 1. Crystallographic data, data collection, and refinement parameters

	9a	**3b**
Empirical formula	$C_{18}H_{12}N_4S_2$	$C_{26}H_{26}N_4S_2$
M_r [g mol^{-1}]	348.45	458.65
Colour, habit	yellow prism	black prism
Crystal size [mm]	0.30 × 0.25 × 0.18	0.29 × 0.22 × 0.18
Crystal system	orthorhombic	monoclinic
Space group	*Pbca* (# 61)	$P2_1/a$ (# 14)
a [Å]	6.736(2)	13.207(3)
b [Å]	24.321(4)	6.337(2)
c [Å]	18.784(3)	28.490(5)
α [°]	90	90
β [°]	90	103.03
γ [°]	90	90
V [Å^3]	3077(1)	2323(1)
Z	8	4
$\rho_{calcd.}$ [g cm^{-3}]	1.504	1.311
μ (Mo-K_α) [mm^{-1}]	0.352[a]	0.251[a]
F(000)	1440	968
Independent rflns up to sinθ/λ = 0.62 Å^{-1}	3015	4755
Rflns observed [$I \geq 2\sigma(I)$]	2591	3302
Refinement method	full-matrix least squares on *F*	
Parameters refined	265	393
R	0.036	0.041
R_w	0.039	0.051

[a] Empirical absorption correction performed (refined from Ψ-scan).

stirred under reflux for 30 min. After cooling to room temperature, the black solution was diluted with chloroform (300 mL), neutralized with saturated aqueous $NaHCO_3$, and washed with water (3 × 100 mL). The organic phase was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The oily residue was chromatographed on silica gel (*n*-hexane/ethyl acetate, 10:4) yielding 2.40 g (80%) **6a** as colourless solid; m.p. 75 °C (*n*-hexane). − IR (KBr): $\tilde{\nu}$ = 3179*s*, 3117*s*, 1573*s*, 1489*s*, 1460*s*, 1426*s*, 1383*s*, 1317*m*, 1286*w*, 1152*w*, 1135*m*, 1099*s*, 1058*s*, 1041*m*, 1018*m*, 907*s*, 865*s*, 735*s*, 723*s*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (3.55), 316 (4.24). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 10.62 (br. s, 1 H, NH), 7.67 (d, ^3J = 3.3 Hz, 1 H, 4-H), 7.13 (d, ^3J = 3.3 Hz, 1 H, 5-H), 6.89−6.86 (m, 1 H, pyrrole-H), 6.73−6.70 (m, 1 H, pyrrole-H), 6.28−6.24 (m, 1 H, pyrrole-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 161.4 (C-2), 142.1 (C-4), 126.5 (C-2′), 120.7 (CH), 116.2 (CH), 110.2 (CH), 110.1 (CH). − EI-MS (70 eV): *m*/*z* (%) = 150 (88) [M$^+$], 149 (2) [M$^+$ − H], 92 (6), 58 (100) [$C_2H_2S^+$]. − HR-MS ($C_7H_6N_2S$): calcd. 150.0252; found 150.0252. − $C_7H_6N_2S$ (150.2): calcd. C 55.98, H 4.02, N 18.64, S 21.35; found C 56.08, H 4.06, N 18.39, S 21.65.

4-*tert*-Butyl-2-(1′*H*-pyrrol-2′-yl)thiazole (6b): To a suspension of 2-pyrrolethiocarboxamide (**4**)[8] (3.78 g, 30.0 mmol) in ethanol (20 mL) was added *tert*-butyl bromomethyl ketone (**5b**) (4.00 mL, 30.0 mmol) in one portion. The reaction mixture immediately became a clear yellow solution and was stirred under reflux for 30 min. During this time a colourless precipitate formed. After cooling at 0 °C, the mixture was filtered and the precipitate was dissolved in diethyl ether (300 mL). The organic layer was neutralized with saturated aqueous $NaHCO_3$ (100 mL), washed with water (2 × 50 mL), and dried with $MgSO_4$. Removal of the solvent under reduced pressure yielded 5.40 g (88%) pure **6b** as colourless solid; m.p. 43 °C (*n*-hexane). − IR (KBr): $\tilde{\nu}$ = 3402*w*, 3188*m*, 3119*m*, 2961*s*, 2904*m*, 2865*m*, 1577*m*, 1506*s*, 1482*s*, 1469*s*, 1428*m*, 1389*m*, 1363*m*, 1234*m*, 1135*w*, 1097*s*, 1020*s*, 948*m*, 890*s*, 875*m*, 728*s*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (3.64), 316 (4.24). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 9.65 (br. s, 1 H, NH), 6.80−6.77 (m, 1 H, pyrrole-H), 6.68 (s, 1 H, 5-H), 6.62−6.60 (m, 1 H, pyrrole-H), 6.22−6.19 (m, 1 H, pyrrole-H), 1.32 (s, 9 H, C(CH_3)$_3$). − ^{13}C NMR ($CDCl_3$, 61 MHz): δ = 166.4 (C), 159.7 (C), 127.1 (C), 119.8 (CH), 110.0 (CH), 108.9 (CH), 107.6 (CH), 34.7 (*C*(CH$_3$)$_3$), 30.0 (C(*C*H$_3$)$_3$). − EI-MS (70 eV): *m*/*z* (%) = 206 (77) [M$^+$], 191 (100) [M$^+$ − CH$_3$], 110 (5), 93 (10), 65 (10), 45 (10). − HR-MS ($C_{11}H_{14}N_2S$): calcd. 206.0878; found 206.0877. − $C_{11}H_{14}N_2S$ (206.3): calcd. C 64.04, H 6.84, N 13.57, S 15.54; found C 63.94, H 6.76, N 13.47, S 15.66.

4-Phenyl-2-(1′*H*-pyrrol-2′-yl)thiazole (6c): To a suspension of 2-pyrrolethiocarboxamide (**4**)[8] (3.78 g, 30.0 mmol) in ethanol (30 mL) was added bromomethyl phenyl ketone (**5c**) (5.97 g, 30.0 mmol) in one portion. The colour of the solution changed immediately from yellow to dark green. The reaction mixture was stirred under reflux for 30 min. After cooling to room temperature, the mixture was diluted with chloroform (300 mL), neutralized with saturated aqueous $NaHCO_3$ (100 mL), and washed with water (3 × 100 mL). The organic layer was dried with $MgSO_4$, filtered, and the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 10:2). Recrystallization of the crude product from toluene yielded 5.83 g (86%) **6c** as colourless needles; m.p. 89−91 °C. − IR (KBr): $\tilde{\nu}$ = 3193*m*, 3106*m*, 3072*w*, 1570*m*, 1484*m*, 1323*w*, 1105*m*, 1071*m*, 1058*m*, 1014*m*, 877*w*, 726*s*, 695*m*, 676*m*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 232 nm (4.09), 264 (4.25), 286 (4.06), 326 (4.17). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 9.54 (br. s, 1 H, NH), 7.90 (dt, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 2 H, phenyl-H), 7.44−7.30 (m, 3 H, phenyl-H), 7.26 (s, 1 H, 5-H), 6.85−6.82 (m, 1 H, pyrrole-H), 6.71−6.68 (m, 1 H, pyrrole-H), 6.27−6.23 (m, 1 H, pyrrole-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 160.4 (C), 155.1 (C), 134.4 (C), 128.7 (CH), 128.1 (CH), 126.7 (C), 126.4 (CH), 120.3 (CH), 110.3 (CH), 110.2 (CH), 109.7 (CH). − EI-MS (70 eV): *m*/*z* (%) = 226 (100) [M$^+$], 134 (74) [$C_8H_6S^+$], 90 (17) [134$^+$ − CS], 89 (14). − HR-MS ($C_{13}H_{10}N_2S$): calcd. 226.0565; found 226.0564. − $C_{13}H_{10}N_2S$ (226.3): calcd. C 69.00, H 4.45, N 12.37, S 14.17; found C 68.99, H 4.54, N 12.21, S 14.39.

General Procedure for the Synthesis of Carbaldehydes 7a−c: To a solution of the corresponding compound **6a−c** (10.0 mmol) in dry THF (150 mL) was added dropwise *n*BuLi (1.6 M solution in *n*-hexane, 13.80 mL, 22.0 mmol) over 15 min at −78 °C. After stirring

for 60 min at −78 °C, a solution of *N*-formylmorpholine (1.95 g, 17.0 mmol) in dry THF (5 mL) was added. In the case of the *tert*-butyl-substituted derivative **6b**, the reaction mixture had to be warmed up to −30 °C for 60 min after addition of *n*BuLi to complete deprotonation. After stirring for an additional 2 h at −78 °C, the mixture was allowed to warm up to room temperature over 6 h and then added to a solution of 2 N HCl (100 mL) with ice cooling. The aqueous phase was neutralized with solid $NaHCO_3$ and extracted with dichloromethane (3 × 100 mL). The combined organic phases were washed with water (100 mL), dried with $MgSO_4$, filtered, and the solvent was evaporated. The crude product was purified by recrystallization.

2-(1′*H*-Pyrrol-2′-yl)thiazole-5-carbaldehyde (7a): Reaction of **6a** (1.50 g, 10.0 mmol) and recrystallization of the crude product from *n*-hexane/ethyl acetate (10:1) furnished 1.50 g (84%) **7a** as yellow flakes; m.p. 157 °C. − IR (KBr): $\tilde{\nu}$ = 3230*m*, 3133*w*, 3088*w*, 2805*w*, 1666*s*, 1565*m*, 1516*m*, 1460*m*, 1237*m*, 1168*m*, 1107*m*, 1022*w*, 906*m*, 726*m*, 667*w*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 240 nm (3.87), 272 (sh, 3.27), 374 (4.42). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 9.97 (s, 1 H, 5-CHO), 9.81 (br. s, 1 H, NH), 8.24 (s, 1 H, 4-H), 7.02−6.99 (m, 1 H, pyrrole-H), 6.92−6.88 (m, 1 H, pyrrole-H), 6.36−6.32 (m, 1 H, pyrrole-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 181.7 (5-CHO), 167.3 (C-2), 152.1 (C-4), 136.6 (C-5), 125.9 (C-2′), 123.2 (CH), 113.4 (CH), 111.6 (CH). − EI-MS (70 eV): *m*/*z* (%) = 178 (100) [M^+], 177 (22) [M^+ − H], 149 (35) [M^+ − CHO], 105 (14), 92 (51), 86 (10). − HR-MS ($C_8H_6N_2OS$): calcd. 178.0201; found 178.0201. − $C_8H_6N_2OS$ (178.2): calcd. C 53.92, H 3.39, N 15.71, S 17.99; found C 53.81, H 3.43, N 15.47, S 18.07.

4-*tert*-Butyl-2-(1′*H*-pyrrol-2′-yl)thiazole-5-carbaldehyde (7b): Reaction of **6b** (2.06 g, 10.0 mmol) and recrystallization of the crude product from *n*-hexane furnished 2.10 g (88%) **7b** as yellow needles; m.p. 142 °C. − IR (KBr): $\tilde{\nu}$ = 3294*m*, 2961*w*, 2927*w*, 2891*w* 1625*s*, 1566*s*, 1456*s*, 1431*m*, 1393*m*, 1310*s*, 1281*m*, 1223*m*, 1126*m*, 1107*m*, 1051*w*, 947*m*, 756*m*, 685*w*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 250 nm (sh, 3.99), 234 (3.66), 374 (4.38). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 10.35 (s, 1 H, 5-CHO), 9.44 (br. s, 1 H, NH), 6.95−6.92 (m, 1 H, pyrrole-H), 6.82−6.78 (m, 1 H, pyrrole-H), 6.29−6.24 (m, 1 H, pyrrole-H), 1.53 [s, 9 H, 4-C(CH_3)$_3$]. − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 183.1 (5-CHO), 172.7 (C), 163.5 (C), 131.7 (C), 126.4 (C), 122.4 (CH), 112.4 (CH), 111.4 (CH), 37.6 [*C*(CH_3)$_3$], 31.9 [C(*C*H_3)$_3$]. − EI-MS (70 eV): *m*/*z* (%) = 234 (100) [M^+], 219 (34) [M^+ − CH_3], 205 (8) [M^+ − CHO], 164 (27), 110 (16), 99 (21), 93 (26), 83 (12), 59 (10), 45 (12). − HR-MS ($C_{12}H_{14}N_2OS$): calcd. 234.0827; found 234.0826. − $C_{12}H_{14}N_2OS$ (234.3): calcd. C 61.51, H 6.02, N 11.95, S 13.68; found C 61.61, H 6.02, N 11.89, S 13.82.

4-Phenyl-2-(1′*H*-pyrrol-2′-yl)thiazole-5-carbaldehyde (7c): Reaction of **6c** (2.26 g, 10.0 mmol) and recrystallization of the crude product from nitromethane furnished 2.20 g (87%) **7c** as yellow crystals; m.p. 140−142 °C. − IR (KBr): $\tilde{\nu}$ = 3201*m*, 3009*w*, 2845*w*, 1635*s*, 1570*m*, 1458*s*, 1425*m*, 1335*s*, 1276*m*, 1124*s*, 1104*m*, 1040*m*, 914*m*, 824*w*, 776*m*, 710*m*, 676*w*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (3.88), 286 (4.23), 382 (4.35). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 9.93 (s, 1 H, 5-CHO), 9.61 (br. s, 1 H, NH), 7.74−7.70 (m, 2 H, phenyl-H), 7.53−7.25 (m, 3 H, phenyl-H), 6.97−6.94 (m, 1 H, pyrrole-H), 6.92−6.89 (m, 1 H, pyrrole-H), 6.34−6.30 (m, 1 H, pyrrole-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 183.8 (5-CHO), 165.2 (C), 163.7 (C), 133.1 (C), 131.2 (C), 130.1 (CH), 129.7 (CH), 128.9 (CH), 126.0 (C), 122.9 (CH), 113.3 (CH), 111.6 (CH). − EI-MS (70 eV): *m*/*z* (%) = 254 (100) [M^+], 254 (60) [M^+ − H], 225 (3) [M^+ − CHO], 134 (50) [$C_8H_6S^+$], 90 (16) [134^+ − CS], 89 (34). − HR-MS ($C_{14}H_{10}N_2OS$): calcd. 254.0514; found 254.0514. − $C_{14}H_{10}N_2OS$ (254.3): calcd. C 66.12, H 3.96, N 11.01, S 12.61; found C 66.25, H 4.08, N 11.06, S 12.93.

General Procedure for the Synthesis of Dicarbaldehydes 8a−c: Freshly distilled phosphoryl chloride (2.30 g, 15.0 mmol) was added dropwise to dry DMF (3 mL) at 0 °C. The mixture was stirred for an additional 15 min at room temperature and then diluted with dry dichloromethane (20 mL). To this suspension a solution of the corresponding carbaldehyde **7a−c** (15.0 mmol) in dry dichloromethane (100−150 mL) was added carefully over 15 min, keeping the temperature at 0 °C. The resulting mixture was stirred for 3 h at room temperature and then added to a stirred solution of NaOAc (20 g) in water (300 mL). After stirring for 30 min, the aqueous phase was neutralized with solid $NaHCO_3$ and extracted with ethyl acetate (6 × 80 mL). The combined organic phases were washed with water (2 × 60 mL), dried with $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude violet product was purified by filtration through a short column packed with silica gel (*n*-hexane/ethyl acetate, 10:4) and recrystallization from nitromethane.

2-(5′-Formyl-1′*H*-pyrrol-2′-yl)thiazole-5-carbaldehyde (8a): Reaction of **7a** (1.78 g, 10.0 mmol) furnished 1.21 g (59%) **8a** as yellow needles; m.p. 188 °C. − IR (KBr): $\tilde{\nu}$ = 3109*w*, 3055*w*, 2986*w*, 2850*w*, 2815*w*, 1664*s*, 1638*s*, 1565*s*, 1511*m*, 1495*w*, 1358*s*, 1225*s*, 1152*s*, 1054*m*, 902*m*, 821*w*, 750*m*, 667*m*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 234 nm (3.87), 258 (3.69), 348 (sh, 4.37), 364 (4.52), 380 (4.46). − ^{1}H NMR ([D_6]DMSO, 250 MHz): δ = 13.23 (br. s, 1 H, NH), 10.06 (s, 1 H, 5-CHO), 9.69 (s, 1 H, 5′-CHO), 8.73 (s, 1 H, 4-H), 7.10−7.08 (m, 2 H, pyrrole-H). − ^{13}C NMR ([D_6]DMSO, 91 MHz): δ = 183.8 (CHO), 180.7 (CHO), 164.5 (C-2), 153.3 (C-4), 138.3 (C), 135.7 (C), 131.5 (C), 119.2 (CH), 113.8 (CH). − EI-MS (70 eV): *m*/*z* (%) = 206 (100) [M^+], 205 (40) [M^+ − H], 177 (20) [M^+ − CHO], 150 (10), 119 (25), 105 (10). − HR-MS ($C_9H_6N_2O_2S$): calcd. 206.0150; found 206.0150. − $C_9H_6N_2O_2S$ (206.2): calcd. C 52.42, H 2.93, N 13.58, S 15.55; found C 52.36, H 2.93, N 13.65, S 15.71.

4-*tert*-Butyl-2-(5′-formyl-1′*H*-pyrrol-2′-yl)thiazole-5-carbaldehyde (8b): Reaction of **7b** (2.34 g, 10.0 mmol) furnished 1.70 g (65%) **8b** as yellow needles; m.p. 161 °C. − IR (KBr): $\tilde{\nu}$ = 3284*m*, 3222*m*, 3113*m*, 2959*w*, 2819*w*, 1659*s*, 1645*s*, 1559*w*, 1400*m*, 1300*m*, 1206*m*, 1057*w*, 951*w*, 797*m*, 729*w*, 683*m*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 238 nm (3.82), 266 (3.53), 368 (4.33), 380 (sh, 4.28). − ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 10.41 (s, 1 H, 5-CHO), 10.12 (br. s, 1 H, NH), 9.65 (s, 1 H, 5′-CHO), 7.01 (dd, ^4J = 1.5 Hz, ^3J = 2.5 Hz, 1 H, pyrrole-H), 6.85 (dd, ^4J = 2.4 Hz, ^3J = 2.5 Hz, 1 H, pyrrole-H), 1.56 [s, 9 H, 4-C(CH_3)$_3$]. − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 183.2 (CHO), 179.8 (CHO), 172.7 (C), 161.3 (C), 134.3 (C), 134.0 (C), 131.9 (C), 121.4 (CH), 112.8 (CH), 37.8 [*C*(CH_3)$_3$], 31.9 [C(*C*H_3)$_3$]. − EI-MS (70 eV); *m*/*z* (%) = 262 (100) [M^+], 247 (39) [M^+ − CH_3], 233 (10) [M^+ − CHO], 192 (33), 121 (12), 99 (23). − HR-MS ($C_{13}H_{14}N_2O_2S$): calcd. 262.0776; found 262.0777. − $C_{13}H_{14}N_2O_2S$ (262.3): calcd. C 59.52, H 5.38, N 10.67, S 12.22; found C 59.51, H 5.26, N 10.71, S 12.25.

4-Phenyl-2-(5-formyl-1′*H*-pyrrol-2′-yl)thiazole-5-carbaldehyde (8c): Reaction of **7c** (2.54 g, 10.0 mmol) furnished 1.27 g (45%) **8c** as yellow needles; m.p. 211 °C. − IR (KBr): $\tilde{\nu}$ = 3268*w*, 3142*w*, 3051*w*, 2830*w*, 1670*s*, 1635*s*, 1564*m*, 1512*w*, 1478*m*, 1395*m*, 1273*m*, 1216*m*, 1145*w*, 917*m*, 765*m*, 691*m*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 248 nm (4.28), 302 (4.13), 373 (4.46), 388 (4.42). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 13.21 (br. s, 1 H, NH), 9.97 (s, 1 H, 5-CHO), 9.71 (s, 1 H, 5′-CHO), 7.95−7.92 (m, 2 H, phenyl-H), 7.60−7.57 (m, 3 H, phenyl-H), 6.14−6.10 (m, 2 H, pyrrole-H). −

^{13}C NMR ($CDCl_3$, 91 MHz): δ = 184.0 (CHO), 180.7 (CHO), 162.8 (C), 162.0 (C), 135.8 (C), 132.9 (C), 132.5 (C), 131.4 (C), 130.2 (CH), 129.9 (CH), 128.8 (CH), 119.3 (CH), 113.9 (CH). − EI-MS (70 eV): *m/z* (%) = 282 (100) [M^+], 281 (52) [$M^+ - H$], 253 (11) [$M^+ - CHO$], 134 (81) [$C_8H_6S^+$], 90 (37) [$134^+ - CS$], 89 (64). − HR-MS ($C_{15}H_{10}N_2O_2S$): calcd. 282.0463; found 282.0463. − $C_{15}H_{10}N_2O_2S$ (282.3): calcd. C 63.82, H 3.57, N 9.92, S 11.36; found C 63.95, H 3.71, N 9.93, S 11.66.

General Procedure for the McMurry Cyclisation of Dialdehydes 8a−c: To a suspension of Zn/Cu couple (4.00 g, 60.0 mmol) in dry THF (200 mL) was added $TiCl_4$ (3.30 mL, 30.0 mmol) by syringe at 0 °C over 15 min. Dry pyridine (1.5 mL) was added and the suspension was refluxed for 2 h. To this freshly prepared and gently refluxing McMurry suspension was added dropwise a solution of the corresponding dicarbaldehyde **8a−c** (3.0 mmol) in dry THF (500 mL) over a period of 60 h. After stirring an additional 5 h at reflux, the dark violet reaction mixture was allowed to cool to room temperature and filtered through Celite. The filtrate was hydrolyzed with 13% ammonia (400 mL) and extracted with dichloromethane (600 mL). The red organic layer was separated, washed with water (2 × 200 mL), dried with $MgSO_4$, filtered, and the solvent evaporated under reduced pressure. To remove the polymeric by-products the residue was filtered through a short column packed with silica gel (*n*-hexane/ethyl acetate, 10:4) and the remaining product was purified by column chromatography on silica gel.

3,20:10,13-Diepithio-6,9:16,19-diimino-1,11-diaza[20]annulene (9a): Reaction of **8a** (0.62 g, 3.0 mmol), column chromatography of the residue (*n*-hexane/ethyl acetate, 10:6) and recrystallisation of crude product from toluene yielded 35 mg (7%) **9a** as yellow prisms; m.p. 250−251 °C. − IR (KBr): $\tilde{\nu}$ = 3399*s*, 3195*m*, 3090*m*, 3014*w*, 1602*m*, 1520*m*, 1421*m*, 1353*m*, 1281*m*, 1201*m*, 1146*m*, 1121*m*, 1040*m*, 1027*m*, 903*w*, 776*s*, 648*m*. −UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 240 nm (sh, 4.09), 268 (4.32), 338 (4.45), 400 (3.62). − ^1H NMR ($CDCl_3$, 360 MHz): δ = 8.41 (br. s, 2 H, NH), 7.50 (s, 2 H, 2,12-H), 6.65 (dd, ^3J = 3.7 Hz, ^4J = 2.7 Hz, 2 H, 8,18-H), 6.48 (s, 4 H, 4,5,14,15-H), 6.19 (dd, ^3J = 3.7 Hz, ^4J = 2.7 Hz, 2 H, 7,17-H); ^1H NMR (C_6D_6, 360 MHz): δ= 8.33 (br. s, 2 H, NH), 7.22 (d, ^4J = 1.0 Hz, 2 H, 2,12-H), 6.63 (dd, ^3J = 3.8 Hz, ^4J = 3.6 Hz, 2 H, pyrrole-H), 5.95 (d, ^3J = 11.1 Hz, 2 H, 5,15-H), 5.93 (dd, ^3J = 3.8 Hz, ^4J = 3.0 Hz, 2 H, pyrrole-H), 5.84 (dd, ^3J = 11.1 Hz, ^4J = 1.0 Hz, 2 H, 4,14-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 162.6 (C), 142.9 (CH), 135.0 (C), 131.1 (C), 129.4 (C), 124.3 (CH), 118.3 (CH), 113.7 (CH), 110.6 (CH). − EI-MS (70 eV): *m/z* (%) = 348 (100) [M^+], 192 (16), 174 (23) [M^{2+}], 142 (13), 129 (11). − HR-MS ($C_{18}H_{12}N_4S_2$): calcd. 348.0503; found 348.0503. − $C_{18}H_{12}N_4S_2$ (348.4): calcd. C 62.05, H 3.47, N 16.07, S 18.41; found C 62.35, H 3.62, N 15.77, S 18.54.

2,12-Di-*tert*-butyl-3,20:10,13-diepithio-6,9:16,19-diimino-1,11-diaza[20]annulene (9b), 2,7-Di-*tert*-butyl-3,20:6,9-diepithio-10,13:16,19-diimino-1,8-diaza[20]annulene (10b), and 2,7,22-Tri-*tert*-butyl-6,9:3,30:20,23-triepithio-10,13:16,19:26,29-triimino-1,8,21-triaza[30]annulene (11b): Reaction of **8b** (0.79 g, 3.0 mmol) and column chromatography of the residue (*n*-hexane/ethyl acetate, 10:1) eluted three fractions containing the crude products **9b**, **10b** and **11b**.

Compound 9b: Chromatography of crude product **9b** (*n*-hexane/ethyl acetate, 10:1) and recrystallisation from *n*-hexane yielded 124 mg (18%) **9b** as yellow prisms; m.p. 136−138 °C. − IR (KBr): $\tilde{\nu}$ = 3433*s*, 3236*m*, 2950*s*, 2925*m*, 2898*m*, 1602*w*, 1484*s*, 1456*m*, 1363*m*, 1289*m*, 1201*m*, 1173*m*, 1045*s*, 1034*s*, 938*w*, 802*s*, 781*s*, 705*m*, 669*m*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 232 nm (4.22), 276 (4.29), 332 (4.37), 408 (3.48). − ^1H NMR ($CDCl_3$, 360 MHz): δ = 7.89 (br. s, 2 H, NH), 6.60 (d, ^3J = 11.2 Hz, 2 H, 4,14-H), 6.47−6.45 (m, 2 H, 8,18-H), 6.45 (d, ^3J = 11.2 Hz, 2 H, 5,15-H), 6.15 (t, *J* = 3.1 Hz, 2 H, 7,17-H), 1.37 [s, 18 H, $C(CH_3)_3$]. − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 162.5 (C), 158.6 (C), 130.6 (C), 128.6 (C), 124.1 (CH), 118.5 (CH), 113.2 (CH), 109.2 (CH), 36.3 [$C(CH_3)_3$], 30.7 [$C(CH_3)_3$]. − EI-MS (70 eV): *m/z* (%) = 460 (53) [M^+], 403 (100) [$M^+ - C(CH_3)_3$], 57 (12) [$C(CH_3)_3^+$]. − HR-MS ($C_{26}H_{28}N_4S_2$): calcd. 460.1755; found 460.1753. − $C_{26}H_{28}N_4S_2$ (460.6): calcd. C 67.79, H 6.13, N 12.16, S 13.92; found C 67.80, H 6.06, N 12.15, S 13.95.

Compound 10b: Chromatography of crude product **10b** (*n*-hexane/ethyl acetate, 10:1) and recrystallisation from *n*-hexane yielded 20 mg (3%) **10b** as yellow crystals; m.p. 131−134 °C − IR (KBr): $\tilde{\nu}$ = 3415*s*, 2962*s*, 2927*m*, 2900*m*, 2865*m*, 1617*w*, 1482*s*, 1457*m*, 1390*m*, 1362*m*, 1292*w*, 1180*m*, 1159*m*, 1035*s*, 950*m*, 820*w*, 779*s*, 668*m*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 (4.19), 262 (4.27), 322 (4.38), 400 (sh, 3.64). − ^1H NMR ($CDCl_3$, 360 MHz): δ = 9.05 (br. s, 2 H, NH), 6.83 (s, 2 H, 4,5-H), 6.48 (dd, ^3J = 3.5 Hz, ^4J = 2.4 Hz, 2 H, pyrrole-H), 6.21 (s, 2 H, 14,15-H), 6.18 (dd, ^3J = 3.5 Hz, ^4J = 2.6 Hz, 2 H, pyrrole-H), 1.39 [s, 18 H, $C(CH_3)_3$]. − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 164.3 (C), 160.5 (C), 131.6 (C), 128.6 (C), 128.5 (C), 123.5 (CH), 117.9 (CH), 113.9 (CH), 109.6 (CH), 36.4 [$C(CH_3)_3$], 30.8 [$C(CH_3)_3$]. − EI-MS (70 eV): *m/z* (%) = 460 (100) [M^+], 445 (3) [$M^+ - CH_3$], 230 (6) [M^{2+}], 57 (12) [$C(CH_3)_3^+$]. − HR-MS ($C_{26}H_{28}N_4S_2$): calcd. 460.1755; found 460.1753 − $C_{26}H_{28}N_4S_2$ (460.6): calcd. C 67.79, H 6.13, N 12.16, S 13.92; found C 67.41, H 6.29, N 11.86, S 13.48.

Compound 11b: Chromatography of crude product **11b** (*n*-hexane/ethyl acetate, 10:3) and recrystallisation from *n*-hexane/toluene (1:1) yielded 36 mg (5%) **11b** as orange crystals; m.p. 209−211 °C. − IR (KBr): $\tilde{\nu}$ = 3431*m*, 3188*w*, 3010*w*, 2955*s*, 2895*m*, 1576*m*, 1559*w*, 1512*m*, 1484*s*, 1458*m*, 1391*m*, 1364*m*, 1210*m*, 1180*s*, 1038*m*, 948*m*, 884*m*, 779*s*, 668*m*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (4.36), 250 (4.28), 358 (4.66), 470 (sh, 3.83). − ^1H NMR ($CDCl_3$, 360 MHz): δ = 8.80 (br. s, 1 H, NH), 8.72 (br. s, 1 H, NH), 8.66 (br. s, 1 H, NH), 7.16 (d, ^3J = 11.3 Hz, 1 H, olefin-H), 6.84 (d, ^3J = 11.3 Hz, 1 H, olefin-H), 6.70 (dd, ^3J = 2.7 Hz, ^4J = 2.4 Hz, 1 H, pyrrole-H), 6.65 (dd, ^3J = 2.5 Hz, ^4J = 2.4 Hz, 1 H, pyrrole-H), 6.51 (d, ^3J = 11.3 Hz, 1 H, olefin-H), 6.47 (dd, ^3J = 2.5 Hz, ^4J = 2.4 Hz, 1 H, pyrrole-H), 6.41 (d, ^3J = 11.3 Hz, 1 H, olefin-H), 6.29−6.24 (m, 4 H), 6.13 (t, *J* = 3.4 Hz, 1 H, pyrrole-H), 1.45 [s, 9 H, $C(CH_3)_3$], 1.43 [s, 9 H, $C(CH_3)_3$], 1.42 [s, 9 H, $C(CH_3)_3$]. − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 162.8 (C), 162.4 (C), 162.3 (C), 156.7 (C), 156.4 (C), 155.9 (C), 131.2 (C), 131.0 (C), 130.2 (C), 128.6 (C), 128.0 (C), 127.9 (C), 124.2 (CH), 123.4 (CH), 123.1 (CH), 122.1 (CH), 118.7 (CH), 117.7 (CH), 117.2 (CH), 113.9 (CH), 112.9 (CH), 111.6 (CH), 110.4 (CH), 110.1 (CH), 36.3 [$C(CH_3)_3$], 36.2 [$C(CH_3)_3$], 36.1 [$C(CH_3)_3$], 30.8 (CH_3), 30.6 (CH_3). − EI-MS (70 eV): *m/z* (%) = 690 (100) [M^+], 633 (9) [$M^+ - C(CH_3)_3$], 345 (24) [M^{2+}]), 57 (12) [$C(CH_3)_3^+$]. − HR-MS ($C_{39}H_{42}N_6S_3$): calcd. 690.2633; found 690.2631.

2,12-Diphenyl-3,20:10,13-diepithio-6,9:16,19-diimino-1,11-diaza-[20]annulene (9c) and 2,7-Diphenyl-3,20:6,9-diepithio-10,13:16,19-diimino-1,8-diaza[20]annulene (10c): Reaction of **8c** (0.79 g, 3.0 mmol) and column chromatography of the residue (*n*-hexane/ethyl acetate, 10:2) eluted two fractions containing the crude products **9c** and **10c**.

Compound 9c: Chromatography of crude product **9c** (*n*-hexane/ethyl acetate, 10:3) and recrystallisation from *n*-hexane/benzene (1:1) yielded 109 mg (14%) **9c** as yellow crystals; m.p. 109−111 °C.

− IR (KBr): $\tilde{\nu}$ = 3426*s*, 3056*w*, 3021*w*, 1601*w*, 1494*m*, 1477*m*, 1457*m*, 1442*m*, 1395*w*, 1323*w*, 1290*w*, 1188*m*, 1033*m*, 921*w*, 785*s*, 770*s*, 693*s*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 234 nm (4.43), 246 (sh, 4.41), 290 (4.45), 344 (4.44), 406 (3.62). − ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 8.52 (br. s, 2 H, NH), 7.72−7.70 (m, 4 H, phenyl-H), 7.43−7.34 (m, 6 H, phenyl-H), 6.71−6.69 (m, 2 H, 8,18-H), 6.62 (d, ^3J = 11.2 Hz, 2 H, 4,14-H), 5.52 (d, ^3J = 11.2 Hz, 2 H, 5,15-H), 6.22 (t, ^3J = 3.1 Hz, 2 H, 7,17-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 162.6 (C), 153.7 (C), 134.2 (C), 131.2 (C), 129.4 (C), 129.1 (C), 128.8 (CH), 128.5 (CH), 128.4 (CH), 124.0 (CH), 119.2 (CH), 113.8 (CH), 110.7 (CH). − EI-MS (70 eV): *m*/*z* (%) = 500 (100) [M^+], 467 (12), 423 (8) [$M^+ - C_6H_5$], 250 (13) [M^{2+}], 121 (50). − HR-MS ($C_{30}H_{20}N_4S_2$): calcd. 500.1129; found 500.1128. − $C_{30}H_{20}N_4S_2$ (500.6): calcd. C 71.97, H 4.03, N 11.18, S 12.81; found C 71.91, H 4.15, N 11.02, S 12.99.

Compound 10c: Chromatography of crude product **10c** (*n*-hexane/ethyl acetate, 10:3) and recrystallisation from *n*-hexane/benzene (1:1) yielded 14 mg (2%) **10c** as yellow crystals; m.p. 106−108 °C. − IR (KBr): $\tilde{\nu}$ = 3409*s*, 3054*w*, 3019*w*, 1596*w*, 1486*m*, 1455*m*, 1446*m*, 1438*m*, 1385*w*, 1296*w*, 1168*m*, 1023*m*, 919*w*, 780*s*, 767*s*, 684*s*. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (4.41), 240 (sh, 4.39), 280 (4.43), 334 (4.43), 400 (3.65). − ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 9.43 (br. s, 2 H, NH), 7.63 (dd, ^3J = 6.8 Hz, ^4J = 1.7 Hz, 4 H, phenyl-H), 7.39−7.25 (m, 6 H, phenyl-H), 6.79 (s, 2 H, 4,5-H), 6.60 (dd, ^3J = 3.3 Hz, ^4J = 2.4 Hz, 2 H, pyrrole-H), 6.24 (s, 2 H, 14,15-H), 6.23−6.21 (m, 2 H, pyrrole-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 157.3 (C), 153.6 (C), 134.2 (C), 130.9 (C), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (C), 126.9 (C), 122.1 (CH), 116.8 (CH), 114.9 (CH), 111.4 (CH). − EI-MS (70 eV): *m*/*z* (%) = 500 (100) [M^+], 467 (2), 423 (1) [$M^+ - C_6H_5$], 250 (10) [M^{2+}], 121 (10). − HR-MS ($C_{30}H_{20}N_4S_2$): calcd. 500.1129; found 500.1128. − $C_{30}H_{20}N_4S_2$ (500.6): calcd. C 71.97, H 4.03, N 11.18, S 12.81; found C 71.71, H 4.09, N 11.35, S 12.51.

General Procedure for the Synthesis of 21,23-Dithia-3,13-diazaporphycenes 3a−c: To a solution of the corresponding dihydroporphycene **9a−c** (0.20 mmol) in THF (50 mL) was added in one portion at −20 °C a solution of DDQ (55 mg, 0.25 mmol) in THF (5 mL). The cooling bath was removed and the mixture stirred for 30 min at room temperature. The blue-green solution was diluted with dichloromethane (200 mL), washed with aqueous $NaHCO_3$ (10%, 3 × 50 mL) and with water (3 × 50 mL). The organic layer was separated, dried with $MgSO_4$, filtered, and the solvent was evaporated at 20 °C under reduced pressure. The black-violet residue was extracted several times with cold *n*-hexane and the resulting violet precipitate was collected by filtration.

21,23-Dithia-3,13-diazaporphycene (3a): Reaction of **9a** (72 mg, 0.20 mmol) and recrystallisation from *n*-hexane/dichloromethane (2:1) yielded 11 mg (17%) **3a** as violet needles; m.p. 186−190 °C (dec.). − UV/Vis (THF): λ_{max} (lg ε) = 388 nm (4.67), 588 (4.32), 684 (3.68), 740 (3.75). − ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 10.41 (s, 2 H, 2,12-H), 10.05 (d, ^3J = 10.8 Hz, 2 H, 10,20-H), 9.37 (d, ^3J = 10.8 Hz, 2 H, 9,19-H), 8.94 (d, ^3J = 4.3 Hz, 2 H, 6,16-H), 8.45 (d, ^3J = 4.3 Hz, 2 H, 7,17-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 159.9 (C), 159.4 (C), 158.7 (C-2,12), 154.9 (C), 141.0 (C-1,11), 134.5 (C-7,17), 127.3 (C-6,16), 124.7 (C-10,20), 122.1 (C-9,19). − FD-MS: *m*/*z* (%) = 346.0 [M^+].

2,12-Di-*tert*-butyl-21,23-dithia-3,13-diazaporphycene (3b): Reaction of **9b** (92 mg, 0.20 mmol) and recrystallisation from benzene yielded 80 mg (87%) **3b** as violet needles; m.p. 223−226 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3095*w*, 3089*w*, 2965*m*, 2923*m*, 2900*w*, 1540*w*, 1475*m*, 1457*m*, 1435*s*, 1400*w*, 1364*m*, 1187*w*, 1015*s*, 1012*m*, 1001*m*, 958*s*, 935*s*, 928*s*, 862*s*, 814*s*, 768*s*. − UV/Vis (THF): λ_{max} (lg ε) = 398 nm (4.81), 594 (4.41), 698 (3.92), 758 (4.22). − ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 10.44 (d, ^3J = 11.2 Hz, 2 H, 10,20-H), 9.29 (d, ^3J = 11.2 Hz, 2 H, 9,19-H), 8.95 (d, ^3J = 4.3 Hz, 2 H, 6,16-H), 8.45 (d, ^3J = 4.3 Hz, 2 H, 7,17-H), 2.22 [s, 8 H, $C(CH_3)_3$]. − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 180.3 (C-2,12), 157.7 (C), 156.7 (C), 155.2 (C), 137.9 (C-1,11), 134.2 (C-7,17), 126.9 (C-6,16), 123.6 (C-10,20), 120.6 (C-9,19), 39.5 [$C(CH_3)_3$], 33.2 [$C(CH_3)_3$]. − FD-MS: *m*/*z* (%) = 458.2 [M^+]. − $C_{26}H_{26}N_4S_2$ (458.6): calcd. C 68.09, H 5.71, N 12.21, S 13.98; found C 68.06, H 5.76, N 12.01, S 14.15.

2,12-Diphenyl-21,23-dithia-3,13-diazaporphycene (3c): Reaction of **9c** (100 mg, 0.20 mmol) and recrystallisation from dichloromethane yielded 84 mg (84%) **3c** as violet needles; m.p. 240−243 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3103*w*, 3081*w*, 3044*w*, 1489*m*, 1448*m*, 1434*s*, 1398*m*, 1339*m*, 1178*w*, 1154*m*, 1125*w*, 1056*s*, 1029*s*, 998*w*, 952*s*, 908*m*, 785*w*, 757*m*, 718*w*, 667*m*. − UV/Vis (THF): λ_{max} (lg ε) = 262 nm (4.35), 410 (4.75), 604 (4.35), 712 (3.96), 776 (4.20). − ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 10.10 (d, ^3J = 11.0 Hz, 2 H, 10,20-H), 9.35 (d, ^3J = 11.0 Hz, 2 H, 9,19-H), 9.03 (d, ^3J = 4.3 Hz, 2 H, 6,16-H), 8.49 (d, ^3J = 4.3 Hz, 2 H, 7,17-H), 8.34−8.36 (m, 4 H, phenyl-H), 7.85−7.73 (m, 6 H, phenyl-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 170.3 (C-2,12), 158.5 (C), 158.1 (C), 155.5 (C), 138.2 (C-1,11), 135.8 (C), 134.7 (C-7,17), 132.2 (CH), 129.9 (CH), 129.2 (CH), 127.4 (C-6,16), 125.4 (C-10,20), 122.4 (C-9,19). − FD-MS: *m*/*z* (%) = 498.1 [M^+]. − $C_{30}H_{18}N_4S_2$ (498.6): calcd. C 72.26, H 3.64, N 11.24, S 12.86; found C 72.00, H 3.77, N 11.27, S 12.66.

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