Palladium-Catalyzed Synthesis of Alkynylated 1,4:5,8:11,14:15,18-Tetrasulfido[20]annulenes

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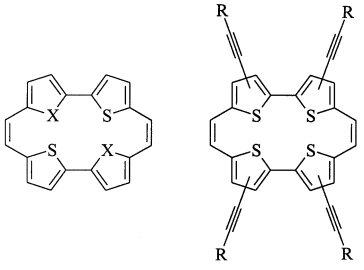
The syntheses of tetraalkynylated tetrasulfido[20]annulenes **2a**–**d** are described. Treatment of the corresponding brominated tetrasulfido[20]annulene **5a** (easily available by McMurry coupling of the brominated 2,2′-bithiophene-5,5′-dicarbaldehydes, **3a**) with various acetylenes in the presence of Pd(II) and Cu(I) in $NH(iPr)_2$ yields acetylenic tetrasulfido[20]annulenes **2a**–**d**.

The syntheses of novel porphyrins, porphycenes, and related conjugated macrocycles are currently the subject of active investigations inter alia for their potential as photosensitizers for biomedical applications[1] such as fluorescence detection, viral inhibition and photodynamic tumor therapy (PDT). In the recent past many attempts have been made to modify the porphyrin ring system to create new chromophores[2]. Prompted by the fundamental work of Vogel and co-workers, who demonstrated the potential use of porphycenes and some of their acetylenic derivatives as PDT agents[3], we investigated the synthesis of sulfur-containing porphycene analogs **1** and observed remarkable changes in the structural and chemical properties of these compounds[4].

Scheme 1



1 **2**

X = NH, S
R = H, Ph, Si(Me)$_3$, Si(*i*Pr)$_3$

2,2′-Bithiophenes, the major structural component of the thiaporphycene skeleton, have been reported as possessing interesting biological activities. Naturally occurring bithiophenes, specifically acetylenic derivatives, show nematocidal, as well as antibiotic, ovicidal, algicidal, larvicidal and antifeedant properties and are phototoxic to some aquatic organisms[5]. Thus, we became interested in the synthesis of alkynylated 1,4:5,8:11,14:15,18-tetrasulfido[20]annulenes **2** in order to combine the properties found in porphycenes and those found in alkynylsubstituted bithiophenes for an approach to a group of macrocycles with high biological activity.

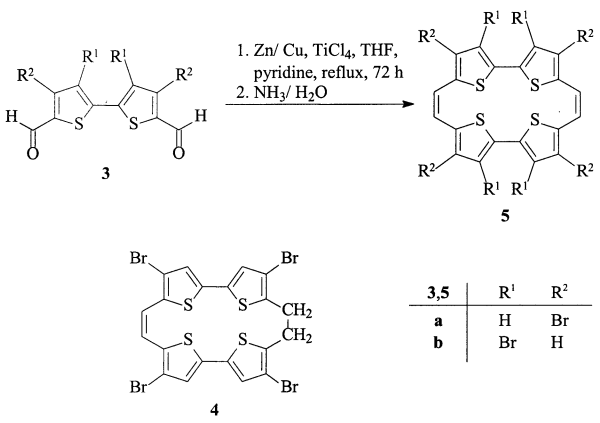
The intermolecular reductive coupling of dicarbonyl compounds with low-valency titanium under McMurry conditions[6] has been established as the most efficient methodology for the preparation of porphycenes and analogous systems[2a][7]. Indeed, we have previously reported the synthesis of alkynylated 2,2′-bithiophene-5,5′-dicarbaldehydes[8], which should be suitable precursors for a McMurry-type cyclisation. However, their dimerisation to the target molecules **2** failed. We therefore decided first to cyclize the brominated 2,2′-bithiophene-5,5′-carbaldehydes **3** and then alkynylate the resulting brominated 1,4:5,8:11,14:15,18-tetrasulfido[20]annulenes **5** by palladium(0)-catalyzed procedures[8][9].

First attempts at the reductive dimerisation of compounds **3** involved reaction conditions used in the synthesis of the unsubstituted tetrasulfido[20]annulene **1** (X = S) as previously reported[4b]. According to this procedure the coupling of 4,4′-dibromo-2,2′-bithiophene-5,5′-dicarbaldehyde (**3a**) with low-valency titanium prepared by treatment of $TiCl_4$ with Zn/Cu pair in the presence of pyridine in THF proceeds under high-dilution conditions and gives, after workup with ammonia, the 2,7,12,17-tetrabromo-9,10-dihydro-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene (**4**) in a yield of 9% (Scheme 2).

The formation of the partially hydrogenated product **4** can be related to observations in the synthesis of other sulfi-

  1434–193X/98/0303–0525 $ 17.50+.50/0

Scheme 2

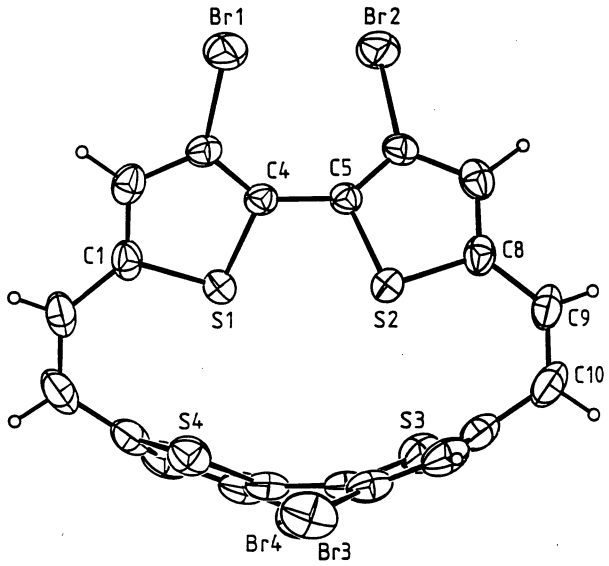


doannulenes which have already been published[4b]. Our experiments revealed that the hydrogenation is caused by a subsequent reaction of the newly formed annulene with nascent hydrogen generated by the reaction of excess Zn/Cu with ammonia. Therefore, removal of the reducing agent from the reaction mixture before the workup with ammonia furnished the desired 2,7,12,17-tetrabromo-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene (**5a**). After a reaction time of 72 h the product was isolated in a yield of 26%, which compares well with those of related conversions[4][10] (Scheme 2). This methodology could also be applied to the synthesis of 3,6,13,16-tetrabromo-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene (**5b**) by dimerisation of the corresponding dicarbaldehyde **3b** (Scheme 2).

The spectroscopic properties (UV/Vis, NMR) of the brominated sulfidoannulenes **5a** and **5b** are similar to those of the nonhalogenated parent compound **1** (X = S) and to those of other thiophene-containing cyclophanes[10]. The spectroscopic data show that **5a** and **5b** do not reflect the typical paratropic behavior of the planar annulene structures of the porphycenes. This fact is confirmed by the crystal structure of **5b** obtained (Figure 1), which is in accordance with the observed nonplanar conformation of the annulene skeleton of **1** (X = S)[4b].

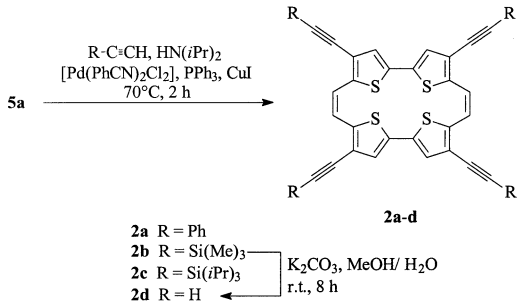
Thus, the structure of **5b** contains one bithiophene unit with anticlinal and one with synclinal arrangement of the sulfur atoms or bromine substituents. In both cases the thiophene rings are twisted; in the anticlinal bithiophene unit they are also bent. The synclinal arranged bithiophene moiety is located approximately in the plane of the double bonds, which is perpendicular to the plane of the synclinal bithiophene group. In contrast to the asymmetrical conformation of **1** (X = S), the structure of **5b** adopts an exact C_2 symmetry in the crystal. The nonplanarity of the annulene skeleton can be explained by the steric demand of the four sulfur atoms. The steric strain between the bithiophene units can be illustrated by the observed short S_1-S_2 distance of 310 pm (van der Waals radius of S 185 pm[11]). The high density of compound **5b** ($D_{calcd.}$ = 2.185 g cm^{-3}) is also remarkable.

Figure 1. Molecular structure of **5b** in side view



The 2,7,12,17-tetrabromo-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene (**5a**) provided an excellent starting material for the preparation of the corresponding tetraalkynylated tetrasulfido[20]annulenes **2a**−**c** (Scheme 3).

Scheme 3



In previous publications we have reported the synthesis of alkynylated 2,2′-bithiophene derivatives[8][9] by palladium(0) catalysis of brominated 2,2′-bithiophenes using the methodology of Whitesides et al.[12], which employs dichlorobis(benzonitrile)palladium(II), triphenylphosphane and copper(I)iodide in boiling diisopropylamine. Identical reaction conditions using **5a** with excess phenyl-, trimethylsilyl- or triisopropylsilylacetylene gave the tetraalkynylated products **2a**−**c** in moderate yields after a reaction time of 2 h (Scheme 3). Only **2c** proved to be stable over extended periods. The terminally unprotected 2,7,12,17-tetraethynyl-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene (**2d**) could easily be prepared by protodesilylation[13] of the trimethylsilyl protected derivative **2b** with aqueous K_2CO_3 in degassed methanol at room temperature in good yield and is the most sensitive derivative of the series (Scheme 3). The spectroscopic properties (UV/Vis, NMR) of the sulfidoannulenes **2a**−**d** are determined by the alkynylated bithiophene subunits and are similar to ethynyl-substituted 2,2′-bithiophenes[8][9].

In conclusion, we have shown that the sequence of palladium(0)-catalyzed alkynylation of brominated bithiophenes is applicable to the preparation of various alkynylated 1,4:5,8:11,14:15,18-tetrasulfido[20]annulenes. The brominated precursors **5** were easily obtained by McMurry coupling of **3** and the formation of hydrogenated byproducts could be explained.

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Experimental Section

General: All reactions were carried out under argon in flame-dried glassware. Diisopropylamine and pyridine were freshly distilled from KOH; THF was distilled from sodium benzophenone before use. Compounds **3a** and **3b** were prepared according to a literature procedure[9]. Silica gel (60-200 mesh) for column chromatography (CC) was obtained from Merck. − Melting points (uncorrected): Reichert melting point microscope. − UV/Vis: Hewlett Packard HP 8453 UV/VIS ChemStation and Hewlett Packard HP 8452A diode array spectrophotometers. − IR: Perkin-Elmer PE 1600 FT-IR spectrophotometer. − NMR: Bruker WM-250 (at 250.13 MHz for ^{1}H and 62.89 MHz for ^{13}C), Bruker AM-360 (at 360.12 MHz for ^{1}H and 90.56MHz for ^{13}C) and Varian XL 300 (at 299.95 MHz for ^{1}H and 75.43 MHz for ^{13}C); δ in ppm rel. to TMS as internal standard. The degree of substitution was determined by *J*-modulated spin-echo experiments. − MS: Varian MAT-311 A, Varian MAT-44 mass spectrometers and JEOL JMS-700 sector field mass spectrometer. Elemental analyses were obtained on a Foss-Heraeus Vario EL.

General Procedure for the Synthesis of Brominated 1,4:5,8:11,14:15,18-Tetrasulfido[20]annulene Derivatives **4** *and* **5a**, **b**: To a suspension of 4.0 g (0.06 mol) of Zn/Cu pair in 200 ml of THF was added 3.3 ml (0.03 mol) of $TiCl_4$ by syringe at 0°C for 30 min. Then 1.5 ml of pyridine was added and the suspension was refluxed for 2 h. To this freshly prepared and gently refluxing McMurry slurry was added dropwise a solution of 1.14 g (3 mmol) of the corresponding brominated 2,2′-bithiophene-5,5′-dicarbaldehyde **3a**, **b** in 600 ml of THF in 3 portions: each portion was added for 14 h and then the reaction mixture was refluxed for 10 h. After 72 h under constant stirring the dark red reaction mixture was allowed to cool to room temperature and was filtered through Celite. The filtrate was quenched with 200 ml of ammonia (25%) and diluted with 750 ml of $CHCl_3$. The organic layer was separated, washed with water and dried with $MgSO_4$. After evaporation under reduced pressure, the residue was separated by chromatography on silica gel.

2,7,12,17-Tetrabromo-1,4:5,8:11,14:15,18-tetrasulfido[20]-annulene-4,9,14,19 {Tetrabromo-[2.0.2.0](2,5)thiophenophane-1,11-diene}[14] (**5a**): Reaction of 1.14 g (3 mmol) of **3a**, column chromatography (*n*-hexane) of residue and recrystallization of crude product from benzene gave 271 mg of **5a** (26%), yellow crystals, m.p. 225−226°C. − IR (KBr): $\tilde{\nu}$ = 071 cm^{-1}, 3022 (CH), 1503, 1471, 1439, 1412, 1358, 1308, 1271, 1242, 1133, 1083, 929, 891, 844, 834, 817, 806, 718, 585. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 284 nm (4.38), 340 (4.28). − ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 7.00 (s, 4 H, 3, 6, 13, 16-H), 6.71 (s, 4 H, 9, 10, 19, 20-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 139.87 (C-4, -5, -14, -15), 136.47 (C-1, -8, -11, -18), 126.94 (C-3, -6, -13, -16), 125.60 (C-9, -10, -19, -20), 113.09 (C-2, -7, -12, -17). − EI-MS (70 eV); *m/z* (%) = 696 (100) [M$^+$], 615 (20) [M$^+$ − ^{81}Br], 536 (20) [M$^+$ − ^{79}Br − ^{81}Br], 455 (10) [M$^+$ − ^{79}Br − 2 ^{81}Br], 376 (30) [M$^+$ − 2 ^{79}Br − 2 ^{81}Br]$^+$, 348 (10) [1/2 M$^+$]. − HR-MS ($C_{20}H_8S_4{}^{79}Br_2{}^{81}Br_2$): calcd. 695.6201; found 695.6200. − $C_{20}H_8S_4Br_4$ (695.6): calcd. C 34.70, H 1.17, S 18.49; found C 34.85, H 1.28, S 18.29.

3,6,13,16-Tetrabromo-1,4:5,8:11,14:15,18-tetrasulfido[20]-annulene {5,8,15,18-Tetrabromo-[2.0.2.0](2,5)thiophenophane-1,11-diene} (**5b**): Reaction of 1.14 g (3 mmol) of **3b**, column chromatography (*n*-hexane) of residue and recrystallization of crude product from benzene gave 92 mg of **5b** (8.8%), yellow crystals, m.p. 302°C. − IR (KBr): $\tilde{\nu}$ = 3067 cm^{-1}, 3016 (CH), 1589, 1549, 1512, 1481, 1373, 1305, 1286, 1243, 1193, 1168, 1140, 1092, 1069, 948, 877, 840, 825, 799, 761, 749, 615, 594, 567, 537, 494. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 276 nm (4.39), 326 (4.17). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.82 (s, 4 H, 2, 7, 12, 17-H), 6.71 (s, 4 H, 9, 10, 19, 20-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 141.96 (C-4, -5, -14, -15), 131.50 (C-2, -7, -12, -17), 125.93 (C-9, -10, -19, -20), 110.49 (C-3, -6, -13, -16). − EI-MS (70 eV); *m/z* (%) = 696 (100) [M$^+$], 615 (10) [M$^+$ − ^{81}Br], 536 (20) [M$^+$ − ^{79}Br − ^{81}Br], 455 (5) [M$^+$ − ^{79}Br − 2 ^{81}Br], 376 (10) [M$^+$ − 2 ^{79}Br − 2 ^{81}Br], 348 (10) [1/2 M$^+$]. − HR-MS ($C_{20}H_8S_4{}^{79}Br_2{}^{81}Br_2$): calcd. 695.6201; found 695.6200. − $C_{20}H_8S_4Br_4$ (695.6): calcd. C 34.70, H 1.17, S 18.49; found C 34.74, H 1.12, S 18.44.

2,7,12,17-Tetrabromo-9,10-dihydro-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene {4,9,14,19-Tetrabromo-[2.0.2.0](2,5)thiophenophan-1-ene} (**4**): In contrast to the general procedure a solution of 1.14 g (3 mmol) of **3b** in 600 ml of THF was added to the McMurry slurry over a period of 48 h. Then the reaction mixture was allowed to cool to room temperature and was quenched with ammonia directly without further filtration. Workup under the conditions described above, column chromatography of residue using petroleum ether (boiling range 40 − 60°C)/$CHCl_3$ (v/v) as eluent and recrystallization of crude product from benzene gave 95 mg of **4** (9.1%), yellow crystals, m.p. 236−237°C. − IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1}, 3022 (CH), 2967, 2920 (CH_2), 1487, 1412, 1318, 1158, 1084, 1000, 874, 818, 784, 772, 709, 645, 566, 555, 498. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 260 nm (4.02), 310 (4.05). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.82 (s, 2 H, 3, 16-H), 6.80 (s, 2 H, 6, 13-H), 6.74 (s, 2 H, 19, 20-H), 3.04 (s, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.87, 138.88, 138.04, 134.28 (C), 127.26, 126.95, 126.32 (CH), 112.58, 108.86 (C−Br), 27.65 (CH_2). − EI-MS (70 eV); *m/z* (%) = 698 (100) [M$^+$], 617 (20) [M$^+$ − ^{81}Br], 538 (5) [M$^+$ − ^{79}Br − ^{81}Br], 457 (5) [M$^+$ − ^{79}Br − 2 ^{81}Br], 378 (5) [M$^+$ − 2 ^{79}Br − 2 ^{81}Br], 349 (30) [1/2 M$^+$]. − HR-MS ($C_{20}H_{10}S_4{}^{79}Br_2{}^{81}Br_2$): calcd. 697.6358; found 697.6356. − $C_{20}H_{10}S_4Br_4$ (697.6): calcd. C 34.41, H 1.44, S 18.37; found C 34.54, H 1.19, S 18.37.

X-ray Structure Analysis of **5b**: Crystals of **5b** suitable for X-ray structure analysis were obtained by slow recrystallization of 70 mg of **5b** from 100 ml of benzene; yellow prisms of crystal size 0.35 × 0.30 × 0.25 mm; intensity data were collected using an Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.071073 nm); crystal system monoclinic, space group *I2/a* (No. 15); cell parameters: *a* = 1334.9(5), *b* = 1074.2(2), *c* = 1510.6(2) pm; β = 102.29(2)°; *Z* = 4; $D_{calcd.}$ = 2.185 g·cm^{-3}; F_{000} = 1328e; μ (Mo-K_α) = 7.92 mm^{-1}; no. of reflections measured 2353 up to (sin θ/ λ)$_{max}$ = 6.4 nm^{-1}; no. of observed reflections with $I \geq 3.0\,\sigma(I)$ 1425; R = 0.035. Structural parameters of non-hydrogen atoms were refined anisotropically according to the full-matrix least-squares technique (refinement on *F*). For further data of crystal structure see ref.[15].

General Procedure for the Synthesis of Tetraalkynylated 1,4:5,8:11,14:15,18-Tetrasulfido[20]annulenes **2a**−**c**: To a solution

of 70 mg (0.1 mmol) of **5a** in 50 ml of freshly distilled diisopropylamine were added 0.1 mmol (39 mg) of dichloro-bis(benzonitrile)palladium(II), 0.2 mmol (53 mg) of triphenylphosphane and 0.1 mmol (19 mg) of copper(I) iodide. An excess of the corresponding acetylene [1 mmol of phenylacetylene (**2a**), trimethylsilylacetylene (**2b**) or triisopropylsilylacetylene (**2c**)] was then added and the solution was stirred at 70°C for 2 h. During this time the solution rapidly turned bright yellow, then yellow brown and finally dark brown, with the formation of a precipitate. The hot suspension was filtered directly, the filtrate was evaporated and the residue was chromatographed on silica gel.

2,7,12,17-Tetrakis(phenylethynyl)-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene {4,9,14,19-Tetrakis(phenylethynyl)-[2.0.2.0](2,5)thiophenophane-1,11-diene} (**2a**): Treatment of **5a** with 0.1 ml of phenylacetylene, column chromatography [petroleum ether (boiling range 40 − 60°C)/$CHCl_3$ 5:1 (v/v)] of residue and recrystallization of crude product from petroleum ether (boiling range 90 − 100°C) gave 45 mg of **2a** (57.7%), yellow crystals, m.p. 152−154°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1}, 3052, 3022 (CH), 2202 (C≡C), 1596, 1499, 1486, 1442, 1245, 1102, 1069, 1027, 913, 830, 786, 753, 720, 688, 548, 536, 526. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 232 nm (4.54), 298 (4.81), 346 (4.42). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.53−7.49 (m, 8 H, C_6H_5), 7.35−7.30 (m, 12 H, C_6H_5), 7.13 (s, 4 H, 3, 6, 13, 16-H), 6.93 (s, 4 H, 9, 10, 19, 20-H). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 143.73, 139.22 (C), 131.63, 128.44, 128.35, 126.47, 125.64 (CH), 123.54, 122.94 (C), 93.08, 83.46 (C≡C). − EI-MS (63 eV); *m/z* (%) = 780 (100) [M^+], 680 (50) [$MH^+ - C_2C_6H_5$]. − HR-MS ($C_{52}H_{28}S_4$): calcd. 780.1074; found 780.1076. − $C_{52}H_{28}S_4$ (780.1): calcd. C 79.99, H 3.62, S 16.39; found C 80.21, H 3.77, S 16.02.

2,7,12,17-Tetrakis[(trimethylsilyl)ethynyl]-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene {4,9,14,19-Tetrakis[(trimethylsilyl)-ethynyl]-[2.0.2.0](2,5)thiophenophane-1,11-diene} (**2b**): Treatment of **5a** with 0.1 ml of trimethylsilylacetylene, column chromatography (hexane) of residue and recrystallization of crude product from ethanol gave 58 mg of **2b** (75.9%), yellow needles, m.p. 218−220°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1}, 3022 (CH), 2957, 2897 (CH_3), 2144 (C≡C), 1654, 1487, 1347, 1319, 1250, 1160, 1104, 1069, 1021, 1005, 987, 842, 760, 716, 701, 678, 646. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 246 nm (4.74), 258 (4.78), 310 (4.51), 344 (4.37).− ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.00 (s, 4 H, 3, 6, 13, 16-H), 6.84 (s, 4 H, 9, 10, 19, 20-H), 0.22 (s, 36 H, CH_3). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 144.73 (C-4, -5, -14, -15), 138.73 (C-1, -8, -11, -18), 126.65 (C-3, -6, -13, -16), 125.62 (C-9, -10, -19, -20), 123.38 (C-2, -7, -12, -17), 98.50, 97.35 (C≡C), −0.22 (CH_3). − EI-MS (70 eV); *m/z* (%) = 764 (50) [M^+], 382 (5) [1/2M^+], 73 (100) [$Si(CH_3)_3$]. − HR-MS ($C_{40}H_{44}S_4Si_4$): calcd.764.1403; found 764.1407. − $C_{40}H_{44}S_4Si_4$ (764.1): calcd. C 62.82, H 5.80, S 16.74; found C 62.55, H 5.81, S 16.61.

2,7,12,17-Tetrakis[(triisopropylsilyl)ethynyl]-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene {4,9,14,19-Tetrakis[(triisopropylsilyl)ethynyl]-[2.0.2.0](2,5)thiophenophane-1,11-diene} (**2c**): Treatment of **5a** with 0.16 ml of triisopropylsilylacetylene, column chromatography (hexane) of residue and recrystallization of crude product from ethanol gave 51 mg of **2c** (46.4%), orange crystals, m.p. 208−209°C. − IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1}, 3019 (CH), 2942, 2890, 2864 [$CH(CH_3)_2$], 2146 (C≡C), 1462, 1383, 1364, 1348, 1321, 1244, 1106, 1072, 1019, 996, 919, 882, 829, 778, 720, 710, 678, 593, 502, 461. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 260 nm (4.83), 312 (4.56), 350 (4.38). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.02 (s, 4 H, 3, 6, 13, 16-H), 6.84 (s, 4 H, 9, 10, 19, 20-H), 1.10 (s, 84 H, $CH(CH_3)_2$). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 144.63 (C-4, -5, -14, -15), 138.93 (C-1, -8, -11, -18), 126.65 (C-3, -6, -13, -16), 125.59 (C-9, -10, -19, -20), 124.01 (C-2, -7, -12, -17), 100.47, 94.93 (C≡C), 18.68 (CH_3), 11.29 (CH). − EI-MS (70 eV); *m/z* (%) = 1100 (100) [M^+], 1014 (5) [$M^+ - 2CH(CH_3)_2$], 900 (5) [$M^+ - Si(CH(CH_3)_2)_3 - CH(CH_3)_2$], 550 (5) [1/2$M^+$], 157 (20) [$Si(CH(CH_3)_2)_3$], 115 (50) [$HSi(CH(CH_3)_2)$]. − HR-MS ($C_{64}H_{92}S_4Si_4$): calcd. 1100.5159; found 1100.5162. − $C_{64}H_{92}S_4Si_4$ (1100.5): calcd. C 69.79, H 8.43, S 11.62; found C 70.05, H 8.47, S 11.32.

2,7,12,17-Tetraethynyl-1,4:5,8:11,14:15,18-tetrasulfido[20]annulene {4,9,14,19-Tetraethynyl-[2.0.2.0](2,5)thiophenophane-1,11-diene} (**2c**): To a suspension of 76 mg (0.1 mmol) of **2b** in 100 ml of deoxygenated methanol (using ultrasonic bath) was added 1 ml of saturated K_2CO_3 solution at room temperature. The mixture was stirred for 8 h. During this time all components dissolved. The solution was diluted with dichloromethane, washed several times with water and dried over $MgSO_4$. The pure product was obtained by simple removal of the solvent at reduced pressure. Recrystallization from petroleum ether (90−110) gave 41 mg of **2d** (86.1%), light yellow needles, m.p. > 60°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (≡CH), 3078, 3022 (CH), 2103 (C≡C), 1577, 1487, 1350, 1253, 1174, 1106, 960, 842, 835, 823, 731, 658, 646, 617, 606, 514. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.05 (s, 4 H, 3, 6, 13, 16-H), 6.90 (s, 4 H, 9, 10, 19, 20-H), 3.21 (s, 4 H, ≡CH). − ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 145.14 (C-4, -5, -14, -15), 138.87 (C-1, -8, -11, -18), 126.90 (C-3, -6, -13, -16), 125.63 (C-9, -10, -19, -20), 122.38 (C-2, -7, -12, -17), 80.97 (≡CH), 77.47 (−C≡). − EI-MS (70 eV); *m/z* (%) = 476 (100) [M^+], 238 (5) [1/2M^+]. − HR-MS ($C_{28}H_{12}S_4$): calcd. 475.9822; found 475.9823. − $C_{28}H_{12}S_4$ (476.0): calcd. C 70.59, H 2.54, S 26.87; found C 70.85, H 2.63, S 26.52.

☆ Dedicated to Professor Dr. *Emanuel Vogel*, University of Cologne, on the occasion of his 70th birthday.

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