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Supporting Information

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Pyrrolo Annelated Tetrathiafulvalenes -The Parent Systems

Bis(pyrrolo[3,4-*d*])tetrathiafulvalene (6): quant. yield; yellow powder from water; mp 215-220°C (decomp); ¹H NMR (DMSO-*d*₆/TMS): δ 6.78 (d, 4 H, *J* = 2.1 Hz, pyrrole H), 11.08 (bs, 2 H, NH); ¹³C NMR (DMSO-*d*₆/TMS): δ 110.56 (pyrrole α-C), 117.30 (=C-C=), 119.52 (C=C); MS-EI: *m/z* (%) 282 (M⁺, 100). Anal. Calcd for C₁₀H₆N₂S₄ (282.41): C 42.53, H 2.14, N 9.92, S 45.41; found: C 42.47, H 2.15, N 9.66, S 45.28.

6·TCNQ: black plates; mp 220°C (decomp.); IR (KBr): 2208 (CN), 2197 (CN) cm⁻¹. Anal calcd for C₂₂H₁₀N₆S₄ (486.61): C 54.30, H 2.07, N 17.27; found: C 53.70, H 2.23, N 16.60.

4,6-Dihydro-5-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (13a): 61% yield; yellow needles from toluene/cyclohexane; mp 234°C (melt with decomp); ¹H NMR (DMSO-*d*₆/TMS): δ 2.40 (s, 3 H, CH₃), 4.47 (s, 4 H, CH₂), 7.46 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.74 (d, 2 H, *J* = 8.3 Hz, Ar-H); ¹³C NMR (DMSO-*d*₆/TMS): δ = 20.99 (CH₃), 53.28 (CH₂), 127.55 (Ar-C), 130.34 (Ar-C), 133.12 (Ar-C), 136.36 (C=C), 144.37 (Ar-C), 218.69 (C=S); MS-EI: *m/z* (%) 329 (M⁺, 35), 173 (M⁺-HTs, 100); IR (KBr): ν 1343 (SO₂), 1158 (SO₂), 1095, 1055 (C=S) cm⁻¹. Anal. Calcd for C₁₂H₁₁NO₂S₄ (329.46): C 43.75, H 3.37, N 4.25, S 38.92; found: C 43.91, H 3.26, N 4.24, S 38.93.

4,6-Dihydro-5-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrol-2-one (13b): 99% yield; off-white needles from toluene/cyclohexane; mp 174-174.5°C; ¹H NMR (CDCl₃/TMS): δ 2.45 (s, 3 H, CH₃), 4.49 (s, 4 H, CH₂), 7.36 (d, 2 H, *J* = 8.2 Hz, Ar-H), 7.75 (d, 2 H, *J* = 8.2 Hz, Ar-H); ¹³C NMR (CDCl₃/TMS): δ 21.47 (CH₃), 53.74 (CH₂), 123.30 (C=C), 127.55 (Ar-C), 130.24 (Ar-C), 133.54 (Ar-C), 144.57 (Ar-C), 193.93 (C=O); MS-EI: *m/z* (%) 313 (M⁺, 14), 158 (M⁺-Ts, 58), 157 (M⁺-HTs, 100); IR (KBr): ν 1687 (C=O), 1343 (SO₂), 1160 (SO₂) cm⁻¹. Anal. Calcd for C₁₂H₁₁NO₃S₃ (313.40): C 45.99, H 3.54, N 4.47, S 30.69; found: C 45.89, H 3.49, N 4.39, S 30.79.

5-Tosyl-(1,3)-dithiolo[4,5-c]pyrrole-2-thione (14a): 75% yield; yellow needles from CH₂Cl₂/cyclohexane; mp 215-215.5°C (melt with decomp); ¹H NMR (CDCl₃/TMS): δ 2.44 (s, 3 H, CH₃), 7.16 (s, 2 H, pyrrole-H), 7.35 (d, 2 H, *J* = 8.4 Hz, Ar-H), 7.79 (d, 2 H, *J* = 8.4 Hz, Ar-H); ¹³C NMR (CDCl₃/TMS): δ 21.62 (CH₃), 110.56 (pyrrole α-C), 127.31 (Ar-C), 128.78 (=C-C=), 130.48 (Ar-C), 135.02 (Ar-C), 146.31 (Ar-C), 218.76 (C=S); MS-EI: *m/z* (%) 327 (M⁺, 72), 155 (Ts⁺, 76), 91 (100); IR (KBr): ν 1372 (SO₂), 1174 (SO₂), 1049 (C=S) cm⁻¹. Anal. Calcd for C₁₂H₉NO₂S₄ (327.45): C 44.02, H 2.77, N 4.28, S 39.16; found: C 44.16, H 2.67, N 4.28, S 39.07.

5-Tosyl-(1,3)-dithiolo[4,5-c]pyrrol-2-one (14b): 95% yield; white powder from CH₂Cl₂; mp 178.5-179°C; ¹H NMR (CDCl₃/TMS): δ 2.43 (s, 3 H, CH₃), 7.22 (s, 2 H, pyrrole-H), 7.34 (d, 2 H, *J* = 8.4 Hz, Ar-H), 7.78 (d, 2 H, *J* = 8.4 Hz, Ar-H); ¹³C NMR (CDCl₃/TMS): δ 21.60 (CH₃), 112.87 (pyrrole α-C), 119.54 (=C-C=), 127.23 (Ar-C), 130.40 (Ar-C), 135.19 (Ar-C), 146.07 (Ar-C), 193.87 (C=O); MS-EI: *m/z* (%) 311 (M⁺, 52), 283 (M⁺-CO, 23), 155 (Ts⁺, 81), 91 (100); IR (KBr): ν 1716 (CO), 1369 (SO₂), 1171 (SO₂) cm⁻¹. Anal. Calcd for C₁₂H₉NO₃S₃ (311.39): C 46.29, H 2.91, N 4.50, S 30.89; found: C 46.38, H 2.81, N 4.56, S 30.85.

(1,3)-Dithiolo[4,5-c]pyrrole-2-thione (15): 84% yield; yellow needles from CH₂Cl₂/petroleum ether (bp 60-80°C); mp 178-178.5 °C; ¹H NMR (DMSO-*d*₆/TMS): δ 7.14 (d, 2 H, *J* = 2.6 Hz, pyrrole-H), 12.05 (bs, 1 H, NH); ¹³C NMR (DMSO-*d*₆/TMS): δ 110.86 (pyrrole α-C), 121.37 (=C-C=), 220.66 (C=S); MS-EI: *m/z* (%) 173 (M⁺, 100); IR (KBr): ν 1055 (C=S) cm⁻¹. Anal. Calcd for C₅H₃N S₄ (173.27): C 34.66, H 1.75, N 8.08, S 55.51; found: C 34.86, H 1.93, N 7.98, S 55.23.

Bis(*N*-tosylpyrrolo[3,4-*d*])tetrathiafulvalene (16): yield 84%; yellow needles from MeOH; mp > 250 °C; ¹H NMR (DMSO-*d*₆/TMS): δ 2.38 (s, 6 H, CH₃), 7.38 (s, 4 H, pyrrole H), 7.45 (d, 4 H, *J* = 8.4 Hz, Ar-H), 7.81 (d, 4 H, *J* = 8.4 Hz, Ar-H); MS-EI: *m/z* (%) 590 (M⁺, 46), 435 (M⁺-Ts, 84), 280 (M⁺-2xTs, 100); IR (KBr): ν 1369 (SO₂), 1173 (SO₂) cm⁻¹. Anal. Calcd for C₂₄H₁₈N₂O₄S₆ (590.78): C 48.79, H 3.07, N 4.74, S 32.56; found: C 48.64, H 2.96, N 4.74, S 32.77.

Bis(*N*-methylpyrrolo[3,4-*d*])tetrathiafulvalene (17a): 82% yield; yellow needles from toluene/petroleum ether (bp 60-80°C); mp 257-258°C (melt with decomp); ¹H NMR (DMSO-*d*₆/TMS): δ 3.60 (s, 6 H, CH₃), 6.75 (s, 4 H, pyrrole H); ¹³C NMR (DMSO-*d*₆/TMS): δ 36.83 (CH₃), 114.40 (pyrrole α-C), 116.90 (=C-C=), 118.86 (C=C); MS-EI: *m/z* (%) 310 (M⁺, 100). Anal. Calcd for C₁₂H₁₀N₂S₄ (310.46): C 46.42, H 3.25, N 9.02, S 41.31; found: C 46.14, H 3.39, N 8.93, S 41.02.

Bis(*N*-butylpyrrolo[3,4-*d*])tetrathiafulvalene (17b): 83% yield; yellow needles from toluene/petroleum ether (bp 60-80°C); mp 190.5-191°C; ¹H NMR (DMSO-*d*₆/TMS): δ 0.87 (t, 6 H, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃), 1.22 (seks, 4 H, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃), 1.64 (quin, 4 H, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃), 3.84 (t, 4 H, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃), 6.81 (s, 4 H, pyrrole H); ¹³C NMR (DMSO-*d*₆/TMS): δ 13.89 (NCH₂CH₂CH₂CH₃), 19.12 (NCH₂CH₂CH₂CH₃), 32.91 (NCH₂CH₂CH₂CH₃), 49.56 (NCH₂CH₂CH₂CH₃), 113.39 (pyrrole α-C), 116.72 (=C-C=), 119.07 (C=C); MS-EI: *m/z* (%) 394 (M⁺, 100), 337 (M⁺ - ⁿBu, 4). Anal. Calcd for C₁₈H₂₂N₂S₄ (394.63): C 54.79, H 5.62, N 7.10, S 32.50; found: C 54.91, H 5.66, N 7.15, S 32.45.

2-{4,5-Bis(methylthio)-1,3-dithiole-2-yliden}-5-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole (18): 57% yield; yellow needles from MeOH; mp 160-160.5°C; ¹H NMR (DMSO-*d*₆/TMS): δ 2.38 (s, 3 H, CH₃), 2.42 (s, 6 H, SCH₃), 7.40 (s, 2 H, pyrrole-H), 7.46 (d, 2 H, *J* = 8.4 Hz, Ar-H), 7.83 (d, 2 H, *J* = 8.4 Hz, Ar-H); ¹³C NMR (DMSO-*d*₆/TMS): δ 18.42 (SCH₃), 21.07 (CH₃), 112.52 (C=C), 112.84 (pyrrole α-C), 117.73 (C=C), 126.14 (=C-C=), 126.21 (CH₃S-C=C-SCH₃), 126.97 (Ar-C), 130.58 (Ar-C), 134.61 (Ar-C), 146.02 (Ar-C); MS-EI: *m/z* (%) 489 (M⁺, 86), 334 (M⁺-Ts, 100); IR (KBr): ν 1373 (SO₂), 1172 (SO₂) cm⁻¹. Anal. Calcd for C₁₇H₁₅NO₂S₇ (489.73): C 41.69, H 3.09, N 2.86, S 45.83; found: C 41.85, H 2.93, N 2.90, S 45.97.

2-{4,5-Bis(methylthio)-1,3-dithiole-2-yliden}-(1,3)-dithiolo[4,5-*c*]pyrrole (19): 92% yield; yellow orange solid from CH₂Cl₂; mp 143.5-145°C (melt with decomp); ¹H NMR (DMSO-*d*₆/TMS): δ 2.44 (s, 6 H, SCH₃), 6.81 (s, 2 H, *J* = 2.9 Hz, pyrrole-H), 11.14 (bs, 1 H, NH); ¹³C NMR (DMSO-*d*₆/TMS): δ 18.39 (SCH₃), 107.27 (C=C), 110.88 (pyrrole α-C), 117.16 (=C-C=), 121.95 (C=C), 126.19 (CH₃S-C=C-SCH₃); MS-EI: *m/z* (%) 335 (M⁺, 100), 320

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(M⁺-CH₃, 24). Anal. Calcd for C₁₀H₉NS₆ (335.55): C 35.80, H 2.70, N 4.17, S 57.33; found: C 35.91, H 2.68, N 4.15, S 57.15.

5-Methyl-2-{4,5-bis(methylthio)-1,3-dithiole-2-yliden}-(1,3)-dithiolo[4,5-c]pyrrole (20a): 93% yield; yellow orange solid from CH₂Cl₂; mp 101-102°C; ¹H NMR (DMSO-*d*₆/TMS): δ 2.43 (s, 6 H, SCH₃), 3.60 (s, 3 H, NCH₃), 6.78 (s, 2 H, pyrrole-H); ¹³C NMR (DMSO-*d*₆/TMS): δ 18.39 (SCH₃), 36.89 (NCH₃), 107.24 (C=C), 114.66 (pyrrole α-C), 116.77 (=C-C=), 121.34 (C=C), 126.24 (CH₃S-C=C-SCH₃); MS-EI: *m/z* (%) 349 (M⁺, 100), 334 (M⁺-CH₃, 21). Anal. Calcd for C₁₁H₁₁NS₆ (349.58): C 37.79, H 3.17, N 4.01, S 55.03; found: C 37.34, H 3.28, N 4.24, S 54.10.

5-Butyl-2-{4,5-bis(methylthio)-1,3-dithiole-2-yliden}-(1,3)-dithiolo[4,5-c]pyrrole (20b): 89% yield; yellow plates from CH₂Cl₂/hexane suitable for X-ray analysis; mp 107.5-108°C; ¹H NMR (CDCl₃/TMS): δ 0.92 (t, 3 H, *J* = 7.3 Hz, NCH₂CH₂CH₂CH₃), 1.30 (seks, 2 H, *J* = 7.3 Hz, NCH₂CH₂CH₂CH₃), 1.70 (quin, 2 H, *J* = 7.3 Hz, NCH₂CH₂CH₂CH₃), 2.42 (s, 6 H, SCH₃), 3.81 (t, 2 H, *J* = 7.3 Hz, NCH₂CH₂CH₂CH₃), 6.45 (s, 2 H, pyrrole-H); ¹³C NMR (CDCl₃/TMS): δ 13.45 (NCH₂CH₂CH₂CH₃), 19.06 (SCH₃), 19.62 (NCH₂CH₂-CH₂CH₃), 33.38 (NCH₂CH₂CH₂CH₃), 50.46 (NCH₂CH₂CH₂CH₃), 110.19 (C=C), 112.46 (pyrrole α-C), 118.51 (=C-C=), 121.32 (C=C), 127.26 (CH₃S-C=C-SCH₃); MS-EI: *m/z* (%) = 391 (M⁺, 100), 376 (M⁺-CH₃, 20). Anal. Calcd for C₁₄H₁₇NS₆ (391.66): C 42.93, H 4.37, N 3.58, S 49.11; found: C 43.03, H 4.34, N 3.69, S 48.99.

X-ray structure analysis of **20b** was performed on a Rigaku AFC6S diffractometer (*Cu Kα* radiation, λ = 1.54178 Å, graphite monochromator, *T* = 296 K, ω-2θ scan, 2θ_{max} = 126°). The structure was solved by a direct method and refined by full-matrix least-squares on *x**F**x*. All calculations were carried out using the crystallographic software package teXsan (Molecular Structure Corporation, 1985 and 1992).

Crystal data: C₁₄H₁₇N₁S₆, *M* = 391.65, yellow plate (0.87 x 0.20 x 0.03 mm³), monoclinic, space group *P*2₁/*a* (#14), *a* = 8.626(3), *b* = 10.507(3), *c* = 20.251(2) Å, β = 94.72(2)°, *V* = 1829.2(7) Å³, *Z* = 4, ρ_{calcd} = 1.422 g/cm³. μ = 68.32 cm⁻¹, *R* = 0.073, *R*_w = 0.068, 2887 measured reflections, 2658 independent reflection, 1551 observed reflections [*I* > 3.0σ(*I*)], 190 refined parameters.

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As shown in Figure 3 the molecular structure of **20b** is nonplanar and consists of three main planes with dihedral angles of 17.6° and 19.3° between the central plane (defined by S1-S4, C9-C10) and the outer planes (defined by S1-S2, C5-C8, N1 and S3-S6, C11-C12), respectively. The bond lengths of C5-C7 (1.38(1) Å), C6-C8 (1.39(1) Å), and C7-C8 (1.41(1) Å) indicate aromatic character in the pyrrole ring as expected.

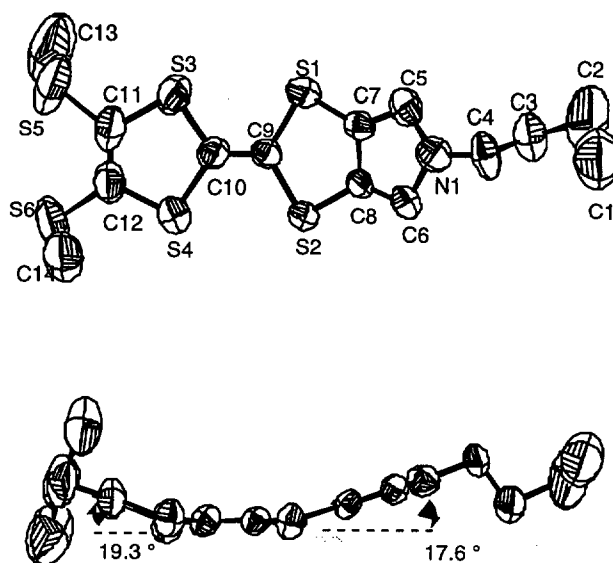


Figure 3. X-ray crystal structure of **20b**