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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); ^{1}H NMR (DMSO-d_6/TMS): δ 6.78 (d, 4 H, J = 2.1 Hz, pyrrole **H**), 11.08 (bs, 2 H, N**H**); ^{13}C 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 $C_{10}H_6N_2S_4$ (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 $C_{22}H_{10}N_6S_4$ (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); ^{1}H NMR (DMSO-d_6/TMS): δ 2.40 (s, 3 H, C**H**$_3$), 4.47 (s, 4 H, C**H**$_2$), 7.46 (d, 2 H, J = 8.3 Hz, Ar-**H**), 7.74 (d, 2 H, J = 8.3 Hz, Ar-**H**); ^{13}C NMR (DMSO-d_6/TMS): δ = 20.99 (**C**H$_3$), 53.28 (**C**H$_2$), 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 (SO$_2$), 1158 (SO$_2$), 1095, 1055 (C=S) cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_2S_4$ (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; ^{1}H NMR (CDCl$_3$/TMS): δ 2.45 (s, 3 H, C**H**$_3$), 4.49 (s, 4 H, C**H**$_2$), 7.36 (d, 2 H, J = 8.2 Hz, Ar-**H**), 7.75 (d, 2 H, J = 8.2 Hz, Ar-**H**); ^{13}C NMR (CDCl$_3$/TMS): δ 21.47 (**C**H$_3$), 53.74 (**C**H$_2$), 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 (SO$_2$), 1160 (SO$_2$) cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_3S_3$ (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 CH_2Cl_2/cyclohexane; mp 215-215.5°C (melt with decomp); ^{1}H NMR ($CDCl_3$/TMS): δ 2.44 (s, 3 H, CH_3), 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**); ^{13}C NMR ($CDCl_3$/TMS): δ 21.62 (**C**H_3), 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 (SO_2), 1174 (SO_2), 1049 (C=S) cm^{-1}. Anal. Calcd for $C_{12}H_9NO_2S_4$ (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 CH_2Cl_2; mp 178.5-179°C; ^{1}H NMR ($CDCl_3$/TMS): δ 2.43 (s, 3 H, CH_3), 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**); ^{13}C NMR ($CDCl_3$/TMS): δ 21.60 (**C**H_3), 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 (SO_2), 1171 (SO_2) cm^{-1}. Anal. Calcd for $C_{12}H_9NO_3S_3$ (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 CH_2Cl_2/petroleum ether (bp 60-80°C); mp 178-178.5 °C; ^{1}H NMR (DMSO-d_6/TMS): δ 7.14 (d, 2 H, J = 2.6 Hz, pyrrole-**H**), 12.05 (bs, 1 H, N**H**); ^{13}C 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 $C_5H_3NS_4$ (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; ^{1}H NMR (DMSO-d_6/TMS): δ 2.38 (s, 6 H, C**H**$_3$), 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 (SO_2), 1173 (SO_2) cm^{-1}. Anal. Calcd for $C_{24}H_{18}N_2O_4S_6$ (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); ^{1}H NMR (DMSO-d_6/TMS): δ 3.60 (s, 6 H, CH_3), 6.75 (s, 4 H, pyrrole **H**); ^{13}C NMR (DMSO-d_6/TMS): δ 36.83 (CH_3), 114.40 (pyrrole α-**C**), 116.90 (=**C**-C=), 118.86 (**C**=C); MS-EI: *m/z* (%) 310 (M^+, 100). Anal. Calcd for $C_{12}H_{10}N_2S_4$ (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; ^{1}H NMR (DMSO-d_6/TMS): δ 0.87 (t, 6 H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.22 (seks, 4 H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.64 (quin, 4 H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 3.84 (t, 4 H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 6.81 (s, 4 H, pyrrole **H**); ^{13}C NMR (DMSO-d_6/TMS): δ 13.89 ($NCH_2CH_2CH_2CH_3$), 19.12 ($NCH_2CH_2CH_2CH_3$), 32.91 ($NCH_2CH_2CH_2CH_3$), 49.56 ($NCH_2CH_2CH_2CH_3$), 113.39 (pyrrole α-**C**), 116.72 (=**C**-C=), 119.07 (**C**=C); MS-EI: *m/z* (%) 394 (M^+, 100), 337 (M^+ - ^{n}Bu, 4). Anal. Calcd for $C_{18}H_{22}N_2S_4$ (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; ^{1}H NMR (DMSO-d_6/TMS): δ 2.38 (s, 3 H, CH_3), 2.42 (s, 6 H, SCH_3), 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**); ^{13}C NMR (DMSO-d_6/TMS): δ 18.42 (SCH_3), 21.07 (CH_3), 112.52 (**C**=C), 112.84 (pyrrole α-**C**), 117.73 (C=**C**), 126.14 (=C-**C**=), 126.21 (CH_3S-**C**=C-SCH_3), 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 (SO_2), 1172 (SO_2) cm^{-1}. Anal. Calcd for $C_{17}H_{15}NO_2S_7$ (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 CH_2Cl_2; mp 143.5-145°C (melt with decomp); ^{1}H NMR (DMSO-d_6/TMS): δ 2.44 (s, 6 H, SCH_3), 6.81 (s, 2 H, J = 2.9 Hz, pyrrole-**H**), 11.14 (bs, 1 H, N**H**); ^{13}C NMR (DMSO-d_6/TMS): δ 18.39 (SCH_3), 107.27 (**C**=C), 110.88 (pyrrole α-**C**), 117.16 (=C-**C**=), 121.95 (C=**C**), 126.19 (CH_3S-**C**=C-SCH_3); MS-EI: *m/z* (%) 335 (M^+, 100), 320

(M^+-CH_3, 24). Anal. Calcd for $C_{10}H_9NS_6$ (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 CH_2Cl_2; mp 101-102°C; ^{1}H NMR (DMSO-d_6/TMS): δ 2.43 (s, 6 H, SC**H**$_3$), 3.60 (s, 3 H, NC**H**$_3$), 6.78 (s, 2 H, pyrrole-**H**); ^{13}C NMR (DMSO-d_6/TMS): δ 18.39 (S**C**H$_3$), 36.89 (N**C**H$_3$), 107.24 (**C**=C), 114.66 (pyrrole α-**C**), 116.77 (=C-**C**=), 121.34 (C=**C**), 126.24 (CH$_3$S-**C**=C-SCH$_3$); MS-EI: *m/z* (%) 349 (M^+, 100), 334 (M^+-CH_3, 21). Anal. Calcd for $C_{11}H_{11}NS_6$ (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 CH_2Cl_2/hexane suitable for X-ray analysis; mp 107.5-108°C; ^{1}H NMR ($CDCl_3$ /TMS): δ 0.92 (t, 3 H, J = 7.3 Hz, NCH$_2$CH$_2$CH$_2$C**H**$_3$), 1.30 (seks, 2 H, J = 7.3 Hz, NCH$_2$CH$_2$C**H**$_2$CH$_3$), 1.70 (quin, 2 H, J = 7.3 Hz, NCH$_2$C**H**$_2$CH$_2$CH$_3$), 2.42 (s, 6 H, SC**H**$_3$), 3.81 (t, 2 H, J = 7.3 Hz, NC**H**$_2$CH$_2$CH$_2$CH$_3$), 6.45 (s, 2 H, pyrrole-**H**); ^{13}C NMR ($CDCl_3$/TMS): δ 13.45 (NCH$_2$CH$_2$CH$_2$**C**H$_3$), 19.06 (S**C**H$_3$), 19.62 (NCH$_2$CH$_2$-**C**H$_2$CH$_3$), 33.38 (NCH$_2$**C**H$_2$CH$_2$CH$_3$), 50.46 (N**C**H$_2$CH$_2$CH$_2$CH$_3$), 110.19 (**C**=C), 112.46 (pyrrole α-**C**), 118.51 (=C-**C**=), 121.32 (C=**C**), 127.26 (CH$_3$S-**C**=C-SCH$_3$); MS-EI: *m/z* (%) = 391 (M^+, 100), 376 (M^+-CH_3, 20). Anal. Calcd for $C_{14}H_{17}NS_6$ (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, $2\theta_{max}$ = 126°). The structure was solved by a direct method and refined by full-matrix least-squares on *xFx*. All calculations were carried out using the crystallographic software package teXsan (Molecular Structure Corporation, **1985** and **1992**).

Crystal data: $C_{14}H_{17}N_1S_6$, M = 391.65, yellow plate (0.87 x 0.20 x 0.03 mm^3), monoclinic, space group $P2_1/a$ (#14), a = 8.626(3), b = 10.507(3), c = 20.251(2) Å, β = 94.72(2)°, V = 1829.2(7) Å^3, Z = 4, ρ_{calcd} = 1.422 g/cm^3. 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.

Revised 06-09-1999

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.

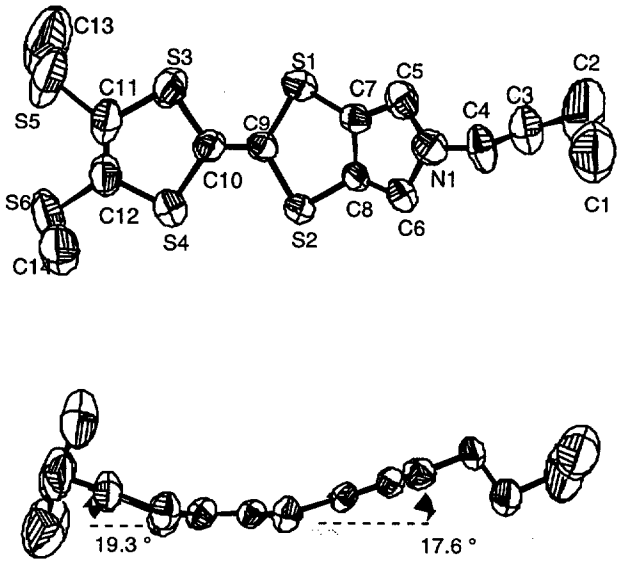

Figure 3. X-ray crystal structure of **20b**