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Bis-substituted Tetrathiapentalenes - Novel Building Blocks for Extended Tetrathiafulvalenes and Conducting Polymers

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Abstract: 1,3,4,6-tetrathiapentalene-2,5-dione (1) reacts in a Wittig-type fashion with aromatic/aliphatic aldehydes **2a** - **h** upon heating in neat triethyl phosphite to bis-substituted tetrathiapentalenes (**3a** - **h**), which can be oligo-/polymerized oxidatively to give vinylogous TTF derivatives or highly conducting, polymeric solids (σ_{RT} = 1 S/cm), respectively. © 1997 Published by Elsevier Science Ltd.

The discovery of interesting solid state properties such as high electrical conductivity or even superconductivity in radical cation salts of tetrathiafulvalene (TTF) derivatives has spurred an intensive search for new donor molecules for the preparation of synthetic metals.[1] Recently, compounds which share structural elements of both, tetrathiafulvalenes and tetrathiapentalenes (TTP) emerged as novel, promising precursors for the preparation of novel organic (super)conductors.[2] Interesting examples in this context are the bis-fused tetrathiafulvalene 2,5-bis(1',3'-dithiole-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) and its derivatives,[3] as well as the parent compound 2,5-di(methylene)-1,3,4,6-tetrathiapentalene (DM-TTP), a yet unknown isomer of TTF.

Owing to their bifunctional character, DM-TTP and its derivatives are important monomeric precursors to the stepwise construction of both extended, oligomeric and polymeric tetrathiafulvalenes, such as those illustrated by general formulae **5** and **6** (cf Scheme 1). BDT-TTP is known to form stable radical cations,[4] whereas DM-TTP is expected to form reactive radical cations upon oxidation which readily dimerize to give eventually 1,2-bis(2,5-ylidene-1,3-dithiolo[4,5-d]1,3-dithiole)ethane. The utility of such oxidative radical coupling reaction has been shown for 1,4-dithiafulvenes,[4-6] and prompted us to investigate the synthetic potential of bifunctional tetrathiapentalenes for the preparation of new, electrically conducting solids.

Here we report on the synthesis, electrochemical and donor properties of 2,5-bis-substituted 1,3,4,6-tetrathiapentalenes, the first representatives of a hitherto unknown class of sulfur heterocycles.

Heating of 1,3,4,6-tetrathiapentalene-2,5-dione (**1**) and aldehydes **2a** - **h** (five equivalents) in triethyl phosphite (60 °C, 48 h; alternatively 120 °C, 2h, Ar atmosphere) afforded the desired products **3a** - **h** as sparingly soluble, yellow powders in fair yields (cf Scheme 1, Table 1 and Note).[7,8] An excess of aldehyde proved necessary to suppress completely the otherwise concomitant autocoupling reaction of **1** to dithiapendione.[7] The reaction is applicable to aromatic and aliphatic aldehydes, whereas ketones and thiopyranone proved unreactive.

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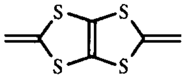
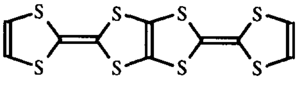
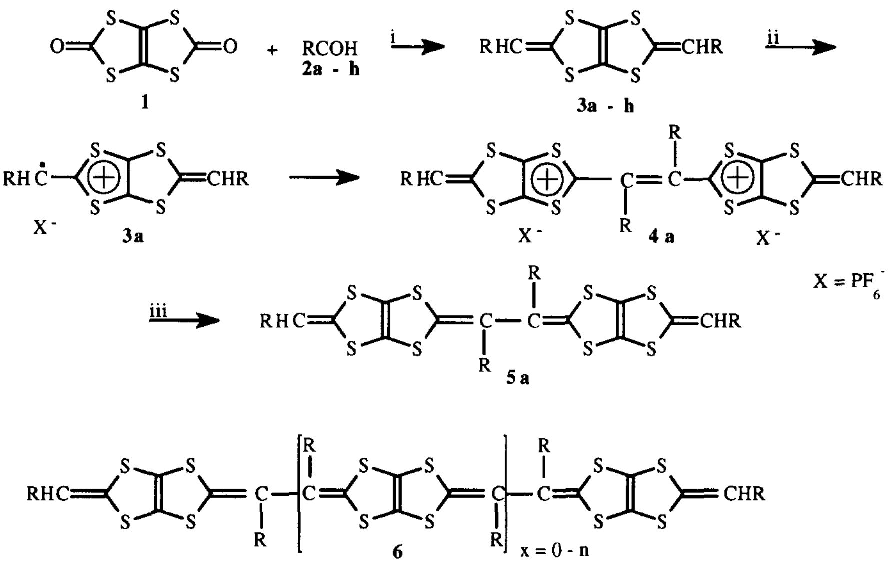


DM-TTP



BDT-TTP



Scheme 1: Synthesis and redox behaviour of bis-substituted tetrathiapentalenes **3a** - **h**.
Reagents and Conditions: i: $P(OEt)_3$/ **2a** - **h** (5 equivalents); 48 h, 60 °C, Ar atmosphere; ii: iodine /dry CH_2Cl_2; 2 h, room temperature or electrochemical process; iii: $NaHSO_3$ solution (40 %)/Aliquat 223®; 3 h, room temp.

Table 1: Synthesis, yields and oxidation peak potentials of **3a** - **h** as determined by cyclic voltammetry.*

Compound	R	Yield [%]	E_{p1} [V]	E_{p2} [V]
2a/3a/4a/5a	$-C_6H_5$	60	1.05	1.76
2b/3b	p-$C_6H_5CF_3$	50	1.08	1.86
2c/3c	p-$C_6H_5OCH_3$	7.5	0.83	1.64
2d/3d	-2-furyl	45	0.92	1.41
2e/3e	(4-methyl)-2-furyl	25	0.9	1.23
2f/3f	2-thienyl	50	1.04	1.41
2g/3g	3-thienyl	30	0.99	1.55
2h/3h	$-CH_2C_6H_5$	30	1.04	1.65

*Conditions: c = 5 10^{-4} M; CH_2Cl_2, 0.1 M n-Bu_4NPF_6, v = 100 mV/s, Pt-electrodes. All values given vs Saturated Calomel Electrode (SCE) as reference. The oxidation peak potential of the redox couple Cp_2Fe^+/Cp_2Fe amounted to + 820 mV vs SCE. All potential values ± 20 mV.

Electrochemical behaviour. Cyclic voltammograms (CV) of **3a** - **h** show two successive, irreversible redox waves. The first oxidation wave corresponds to a one-electron transfer as indicated by coulometry and thus can be assigned to the formation of the monoradical cation $\mathbf{3}^{\bullet+}$. The second redox step involves several electron transfer processes, which results in a complex electrochemical behaviour. Multisweep CV provide clear evidence for follow-up reactions of the monoradical species $\mathbf{3}^{\bullet+}$.[8] Compared to the reversible redox behaviour typically found for TTF derivatives, [9] radical cations of **3a** - **h** are clearly destabilized. The oxidation peak potentials are considerably shifted toward more positive values, and reflect to some extent the electron withdrawing/electron donating effects of the substituents R (Table 1).

The observed deposition of black, conducting films on the working electrode upon continued potential cycling is presumed to originate from the dimerization of monoradical cations $\mathbf{3}^{\bullet+}$, and subsequent dehydrogenation to intermediates **4**, followed by further oligo-/polymerization steps to compounds of generalized formula **6** (cf Scheme 1). The isolation of the extended TTF-derivative **5a** upon oxidation of **3a** with iodine followed by reduction with sulfite in fair yield (10 %) provides strong support for this assumption. A very similar mechanism has been discussed lately for the dimerization of 1,4 dithiafulvenes. [6,10]

Donor Properties. Heating of donor molecules **3a** - **h** with the electron acceptor tetracyanoquinodimethane (TCNQ) in chlorobenzene (CB) or o-dichlorobenzene (DCB) yielded a variety of CT-complexes, the electrical conductivities and charge transfer numbers Z of some of which are summarized in Table 2.

Table 2: Compositions, Charge Transfer and Electrical Conductivities (298 K) of CT complexes.

CT complex	Composition* (Donor : TCNQ)	Charge transfer Z (ν-CN [cm $^{-1}$])[11]	Conductivity [S/cm]**
7	**3a** (1 : 2)/CB	0 (2226)	$\leq 10^{-8}$
8	**3a** (1 : 2)/DCB	0.14 (2221)	2×10^{-3}
9	**3a** (2 : 3)/DCB	0 (2226) and 0.7 (2197)	5×10^{-5}
10	**3f** (1 : 1)/DCB	0.4 (2208)	3×10^{-4}
11	**3g** (1 : 1)/DCB	0.6 (2200)	$\leq 10^{-8}$

*as determined by elemental analyses. **as determined by four-probe measurements on compaction samples.

The IR spectrum of compound **9** shows two different CN stretch vibrations with an intensity ratio of about 3:1 which points to the presence of two different types of TCNQ molecules. This view is corroborated by the ESR spectrum of **9** which displays two superimposed signals (5.7 G and 1.1 G; g = 2.0033), by contrast to the symmetric signals observed for **7** and **8** with identical linewidths (0.8 G; g = 2.0035). The relatively poor conductivities of the CT-complexes **7** - **11**, reflect both the comparatively low donicity as well as the non-planarity of the donor molecules which prevent an optimal orbital overlap with the planar acceptor TCNQ.[12]

Interestingly, films obtained upon electropolymerization of **3a**, **c** - **g**, either by repeated potential cycling or potentiostatic electrolysis, exhibit relatively high electrical conductivities of 10^{-1} to 1 S/cm (four-probe measurements at ambient temperature).

In conclusion, a new class of tetrathiapentalene derivatives has been synthesized in an operationally simple one-step reaction, their electrochemical behaviour and donor properties have been investigated. The bifunctional compounds **3a** - **h** are promising monomeric precursors to new electrically conducting, polymeric solids, and to the stepwise construction of extended, vinylogous TTF derivatives.

References and Notes

1. For a recent review see: Proc. Int. Conf. *Science and Technol. Synth. Metals (ICSM '94)*; Elsevier: Seoul, Korea, 1994, A.J. Heeger (Ed.), *Synth. Met.* , **1995**, *69 - 71*, 1 - 2308.
2. Misaki, Y., Yamabe, T., Higuchi, N., Fujiwara, H., Mori, T., Mori, H., Tanaka, S., *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 1222 - 1225.
3. Misaki, Y., Nishikawa, H., Kawakami, K., Uehara, T. ,Yamabe, T., *Tetrahedron Lett.*, **1992**, *33*, 4321 - 4324.
4. Kirmse, W., Horner, L., *Liebigs Ann. Chem.*, **1958**, *614*, 4 - 18.
5. Mayer, K., Kröber, H., *J. Prakt. Chem.*, **1974**, *316*, 907 - 912.
6. Lorcy, D., Carlier, R., Robert, A., Tallec, A., Maguères, P. L. , Ouahab, L., *J. Org. Chem.*, **1995**, *60*, 2443 - 2447.
7. Schumaker, R. R., Engler, E. M., *J. Am. Chem. Soc.*, **1977**, *99*, 5521 - 5522.
8. Müller, H. Thesis, Technical University of Munich, 1991. A detailed discussion of the electrochemical properties will be published elsewhere.
9. Tatemitsu, H., Nishikawa, E., Sakata, Y., Misumi, S., *J. Chem. Soc. Chem. Comm.*, **1985**, 106 - 107.
10. Hapiot, P., Lorcy, D., Tallec, A., Charlier, R., Robert, A., *J. Phys. Chem.*, **1996**, *100*, 14823 - 14827.
11. Chappell, J. S., Bloch, A. N., Bryden, W. A., Maxfield, M., Poehler, T. O., Cowan, D. O., *J. Am. Chem. Soc.*, **1981**, *103*, 2442 - 2443.

12. Molecular modelling performed with the program package AM 1 predicts a planar central TTP-moiety and angles of ± 33 ° between the central molecular (TTP) plane and the aromatic substituents with equal probability for both staggered/eclipsed conformations, when viewed along the long molecular axis.

Analytical and spectroscopic data for compounds **3a** - **h**, and **5a:**
2,5-Dibenzylidene-[1,3]dithiolo-[4,5-d]1,3-dithiole (**3a**): mp 191.5 -192 °C; IR (KBr): 3099, 3078, 3048, 2988, 1555, 818, 743, 686, 516 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.65 (s, 2 H, =C$\underline{H}$-), 7.09 - 7.29 (m, 10 H_{arom}); MS (EI) m/z (%) 355.8 (100) [M^+]; Anal. calc. for $C_{18}H_{12}S_4$: C, 60.64; H, 3.39; S, 35.97. Found: C, 60.42; H, 3.6; S, 36.32. 2,5-Bis(4-trifluoromethyl)benzylidene)-[1,3]dithiolo-[4,5-d]1,3-dithiole (**3b**): mp 220 °C; IR (KBr): 1612, 1578, 1558, 1410, 1322 (vs, br), 1180, 1118 (vs, br), 1069, 855 cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 6.68 (s, 2 H, =C$\underline{H}$-), 7.30 - 7.65 (m, 8 H_{arom}); MS (EI) m/z (%) 491.9 (100) [M^+]. Anal. calc. for $C_{20}H_{10}S_4F_6$: C, 48.77; H, 2.05; S, 26.05. Found: C, 48.72; H, 1.91; S, 26.04. 2,5-Bis(4-methoxybenzylidene-[1,3]dithiolo-[4,5-d]1,3-dithiole (**3c**): mp 235 °C; IR (KBr): 2971, 1604, 1559, 1506, 1252, 1033, 840 cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 3.76 (s, -OC$\underline{H}_3$), 6.56 (s, 2 H, =C$\underline{H}$-), 6.87 - 7.16 (m, 8 H_{arom}); MS (EI) m/z (%) 416.2 (100) [M^+]. Anal calc. for $C_{20}H_{16}S_4O_2$: C, 57.66; H, 3.87; S, 30.78. Found: C, 57.51; H, 3.90; S, 30.86. 2,5-Di(2-furylidene)-[1,3]dithiolo-[4,5-d]1,3-dithiole (**3d**): mp 194 °C; IR (KBr): 3110, 1599, 1575, 1483, 1028, 734 cm^{-1}; ^{1}H NMR (d_6-DMSO): δ 6.27 (m_c, 2 H_{arom}), 6.51 (m_c, 2 H_{arom}), 6.83 (s, 2 H, =C$\underline{H}$-, 7.73 (m_c, 2 H_{arom}), MS (EI) m/z (%) 336 (100) [M^+]. Anal. calc. for $C_{14}H_8S_4O_2$: C, 49.98; H, 2.40; S, 38.11. Found: C, 50.24; H, 2.43; S, 37.99. 2,5-Di(2-thienylidene)-[1,3]dithiolo-[4,5-d]1,3-dithiole (**3e**): mp 230 °C; IR (KBr): 1560, 850, 837, 825 684 cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 6.83 (s, 2 H, =C$\underline{H}$), 6.83 - 6.92 (m, 2 H_{arom}), 7.04 - 7.08 (m, 2H_{arom}), 7.32 - 7.37 (m, 2 H_{arom}), MS (EI) m/z (%) 368 (100) [M^+]. Anal. calc. for $C_{14}H_8S_6$: C, 45.62; H, 2.19; S, 52.19. Found: C, 45.11; H, 2.09; S, 50.76.2,5-Di(3-thienylidene)-[1,3]dithiolo-[4,5-d]1,3-dithiole (**3f**): mp 220 °C; IR (KBr): 3089, 1570, 821, 811, 764, 715, 690, 620 cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 6.66 (s, 2 H, =C$\underline{H}$-), 7.02 - 7.11 (m, 4 H_{arom}), 7.31 - 7.35 (m, 2 H_{arom}), MS (EI) m/z (%) 368 (100) [M^+]. Anal. calc. for $C_{14}H_8S_6$: C, 45.62; H, 2.19; S, 52.19. Found: C, 44.74; H, 2.05; S, 51.39. 2,5-Bis(4-methylfur-2-ylidene)-[1,3]dithiolo-[4,5-d]1,3-dithiole (**3g**): mp 138.5 °C; IR (KBr): 2919, 1599, 1523, 1435, 1232, 1174, 1027, 802, 716 cm^{-1}; ^{1}H NMR (d_6-DMSO): δ 2.27 (s, -C$\underline{H}_3$), 6.05 (AA'BB' d, 2 H_{arom}, J = 3.4 Hz), 6.26 (AA'BB' d, 2H_{arom}, J = 3.4 Hz), 6.75 (s, 2 H, =C$\underline{H}$-); MS (EI) m/z (%) 364 (100) [M^+]. Anal. calc. for $C_{16}H_{12}S_4O_2$: C, 52.72; H, 3.32; S, 35.18. Found: C, 52.41; H, 3.36; S, 34.81. 2,5-Di(benzylylidene)-[1,3]dithiolo-[4,5-d]1,3-dithiole (**3h**): mp 142 °C; IR (KBr): 3061, 3023, 1602, 1584, 1494, 1451, 744, 699 cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 3.26 (d, ^{3}J = 7.48, 4 H, -C$\underline{H}_2$-), 5.72 (t, ^{3}J = 7.48, 2 H, =C$\underline{H}$-), 7.1 - 7.4 (m, 10 H_{arom}), MS (EI) (m/z (%) 384 (90) [M^+]; Anal. calc. for $C_{20}H_{16}S_4$: C, 62.46; H, 4.19; S, 33.3. Found: C, 62.15; H, 4.21; S, 33.3. 1,2-bis(5-benzylidene-[1,3]dithiolo-[4,5-d]1,3-dithiole-2-ylidene)1,2-diphenylethane (**5a**): mp 125 °C; IR (KBr): 3050, 2921, 1685, 1594, 1577, 1555, 1490, 1440, 744, 694 cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 6.60 (s, 2H, =C$\underline{H}$-), 7.16 - 7.42 (m, 20 H_{arom}); HR-MS (FAB) m/z (%) calc. for $C_{36}H_{22}{}^{32}S_8$: 709.9487, found: 709.9481.

For the CT-complexes **7** - **11** satisfactory elemental analyses were obtained (C + 0.39, H + 0.17).

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