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Novel Benzo[d]1,2,3-trithioles and their Hexachloroantimonates derived from Benzenehexathiol

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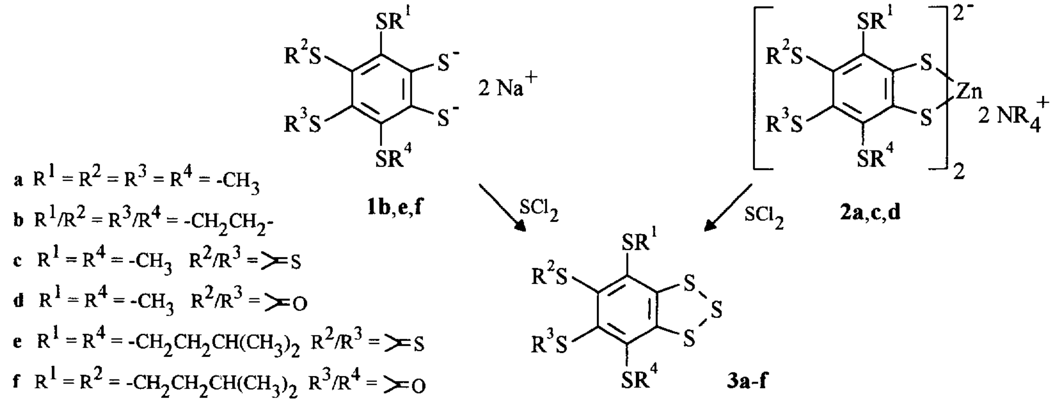
Abstract: Various substituted benzo-mono-, bis-, and tris-1,2,3-trithioles were synthesized by reaction of the corresponding thiolates with sulfur dichloride. Benzo-bis(trithiolo)pentathiepin was isolated as a by-product. These trithioles form with cyanide dibenzo[c,g]1,2,5,6-tetrathiocines and afforded with antimony pentachloride stable radical cations. Some EPR and conductivity data are reported.

Benzo annellated 1,2,3-trithioles [1,2,3] are of interest in regard to their formation, stability and potential ability to form radical cations by oxidation. These trithiole radical salts may become important as new organic magnetic and/or electrical conducting materials. We report about the synthesis and properties of a series of benzo-1,2,3-trithioles derived from benzenehexathiol and their remarkably stable trithiolium hexachloroantimonates. Furthermore, a new type of tetrathiafulvalenes (TTF) was designed by combining the dibenzo-TTF unit with 1,2,3-trithiole structural elements.

Benzo[d]1,2,3-trithioles

Preparation

Starting materials for the synthesis of benzotrithioles **3** were the benzo-1,2-dithiolates **1b,e,f** or their zinc complexes **2a,c,d** obtained by cleavage of the corresponding benzo-1,3-dithiole-2-ones and -2-thiones [3,4]. Ring closure with sulfur dichloride afforded the desired novel per-sulfur substituted benzo-1,2,3-trithioles **3**.

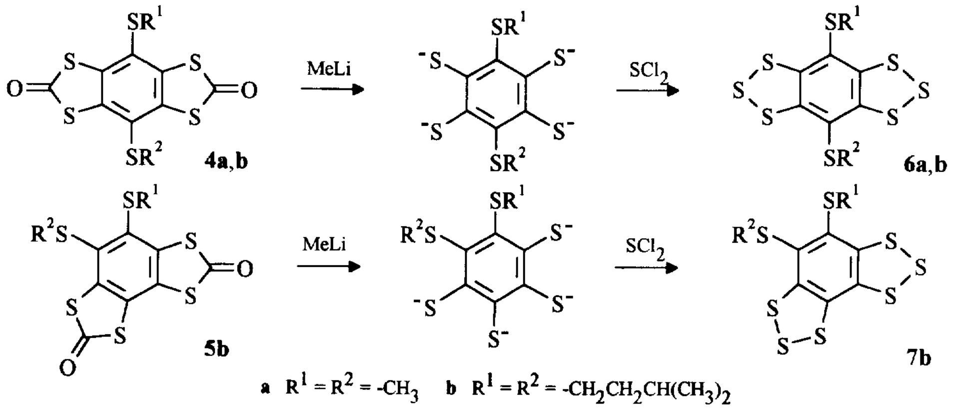


a $R^1 = R^2 = R^3 = R^4 = -CH_3$
b $R^1/R^2 = R^3/R^4 = -CH_2CH_2-$
c $R^1 = R^4 = -CH_3$ $R^2/R^3 = {>}{=}S$
d $R^1 = R^4 = -CH_3$ $R^2/R^3 = {>}{=}O$
e $R^1 = R^4 = -CH_2CH_2CH(CH_3)_2$ $R^2/R^3 = {>}{=}S$
f $R^1 = R^2 = -CH_2CH_2CH(CH_3)_2$ $R^3/R^4 = {>}{=}O$

1b,e,f **2a,c,d** **3a-f**

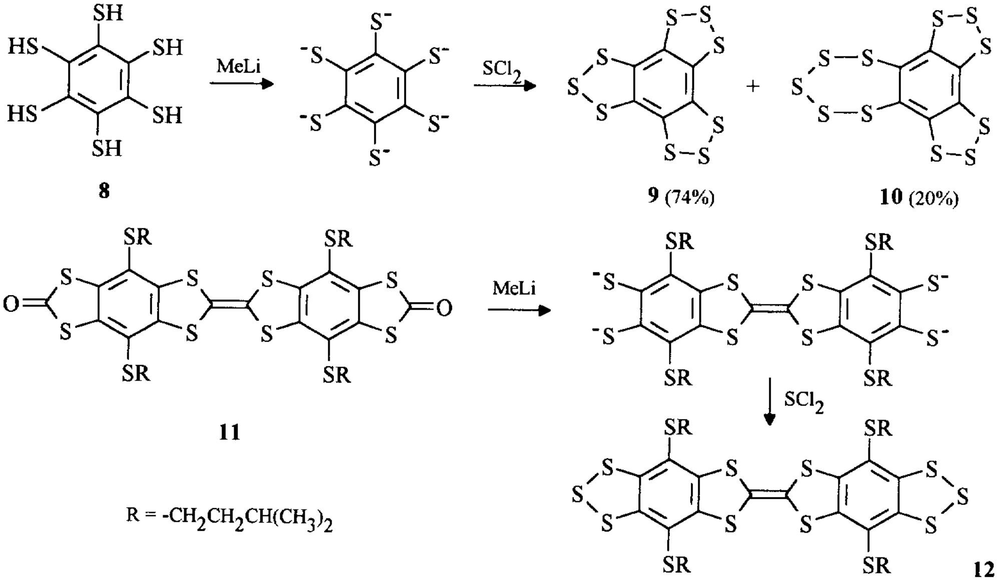
Scheme 1

The benzo-bis-trithioles **6** and **7** were obtained by repeated nucleophilic ring opening of the tetrathiaindacenediones **4** and **5** with methyllithium and subsequent reaction of the generated tetrathiolates with sulfur dichloride. These reactions were carried out in anhydrous tetrahydrofuran under nitrogen at -10°C.



Scheme 2

The new "carbon sulfide" [5,6] benzo[1,2-d][3,4-d'][5,6-d'']-tris-1,2,3-trithiole (C_6S_9) **9** was directly made from lithiumbenzenehexathiolate. This reaction path requires anhydrous lithiumhexathiolate, available by protonation to hexamercaptobenzene **8** [7], drying and deprotonation with methyllithium. In tetrahydrofuran treatment of this product with sulfur dichloride led to the crude product of **9** (Scheme 3). We isolated benzo[3,4-d][5,6-d']-bis-1,2,3-trithiolo-[1,2-d'']pentathiepin **10** (C_6S_{11}) as by-product by extraction with carbon disulfide and removal of the solvent. Both compounds melt under decomposition (**9**: mp. 195-200°C, **10**: mp. 98-102°C) and only a few weak absorptions were found in the IR spectra. The insoluble tristrithiole **9** possesses C_3 symmetry, and is thus expected to have an interesting chemistry (for the structure of benzotrithioles compare [1b,c,2,3]).



Scheme 3

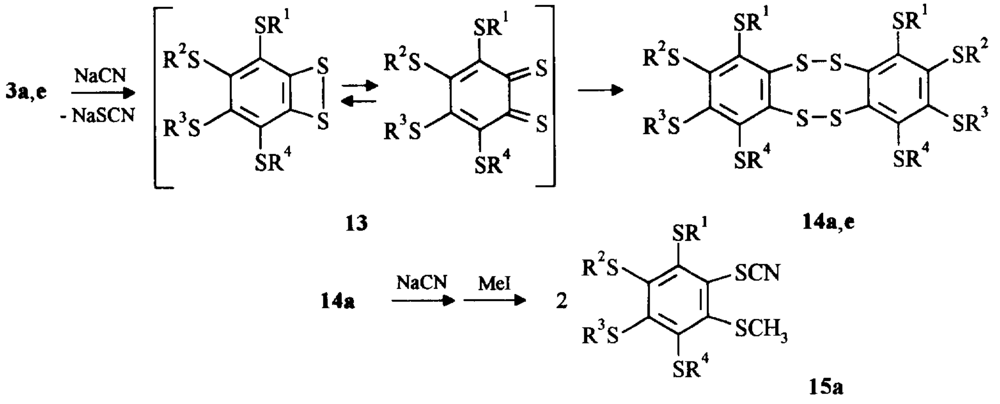
We also synthesized the tetrathiafulvalene **12**, the first example of a new class of a benzo-TTF containing two 1,2,3-trithiole groups. **12** is an interesting donor molecule with potential intermolecular interactions in the solid state [8]. It was made from the TTF **11** [4a] analogous to the synthesis of the bistrithioles **6** and **7** with methyllithium and sulfur dichloride (Scheme 4). This modified TTF in combination with reversible redox units opens up a wide variety of new electron donor substances [9].

Properties

The benzo-1,2,3-trithioles are stable under normal conditions. This stability is underlined by their mass spectroscopic fragmentation patterns (EI): All compounds show molecular ion peaks. In the case of the thioalkylated trithioles the base peaks indicate that the first bond breaking takes place at the sulfur-alkyl bonds. Accordingly, the *iso*-pentyl substituted derivatives first eliminate two molecules of pentene before the sulfur-sulfur bonds are cleaved. The tristrithiole **9** and the pentathiepin **10** fragment under sulfur elimination. Likewise sublimation of **9** yielded only sulfur. The benzotrithioles are orange colored compounds with a characteristic UV-Vis absorption at 310 nm (1,2 dichloroethane) and well soluble (except **9** and **10**) in halogenated hydrocarbons like chloroform and dichloroethane.

Nucleophilic Elimination of Sulfur

We tried to find a method for the controllable elimination of one sulfur atom from a trithiole to generate benzodithietes. Therefore, the trithioles **3** were treated with one equivalent of sodium cyanide in acetonitrile affording quantitatively the precipitating dibenzo[c,g]1,2,5,6-tetrathiocines **14** and thiocyanate. We suppose an equilibrium of the benzodithiete/o-dithiobenzoquinone **13** [10] as intermediates in the first reaction step. Compound **14** should originate from these intermediates by dimerization [3].



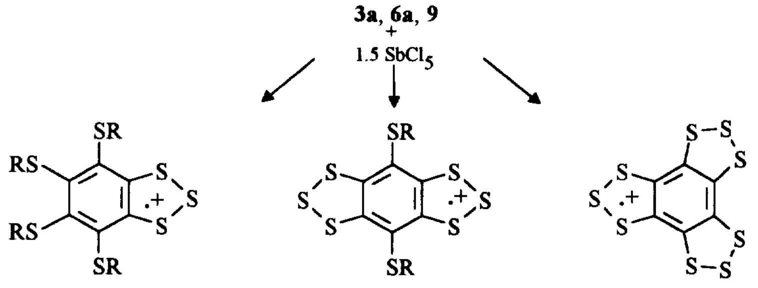
Scheme 4

However, preparation of tetrathiocines according to this protocol is less favorable than the oxidation of dithiolates [3]. Moreover, the tetrathiocines **14** undergo reaction with cyanide to form a mixture of five compounds after methylation yielding benzothiocyanate **15** as main product.

Trithiolium Radical Cations

Preparation

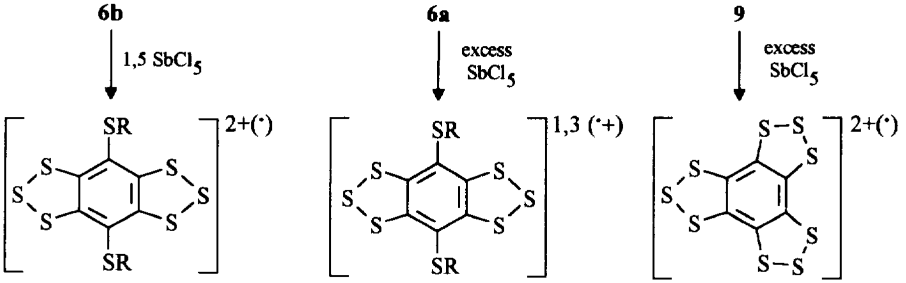
The benzo-1,2,3-trithioles are week electron donors. That means, they should be oxidizable by strong electron acceptors to give radical cations. Attempts to use 2,3-dichloro-5,6-dicyano-p-benzoquinone [DDQ, $E^1_{1/2} = 0.56V$[11]] as oxidizing agent failed. In agreement with these facts the cyclic voltammogram of **3a** shows a reversible oxidation potential of $E_{1/2}$ = 1.13V (SCE). The benzo annellated trithiolium salts are accessible by adding antimony pentachloride to a solution of the trithioles in anhydrous 1,2-dichloroethane at room temperature. Immediately the solution turns dark green and - dependent on their solubility - benzo-1,2,3-trithiolium salts **16** were precipitated. These salts were filtered off and washed with dichloroethane. Particularly in the case of *iso*-pentyl substituted derivatives it was necessary to remove most of the solvent and to crystallize the trithiolium radicals by dropwise addition of hexane.



16a R = -CH$_3$ **16b** **16c**

Scheme 5

The degree of oxidation of **9** and of the bistrithioles **6** was adjustable by the amount of added antimony pentachloride, except in the case of **6b**: even the treatment of **6b** with one equivalent of the oxidant (1.5 mol SbCl$_5$ per trithiole unit to be oxidized) gave the dication **16d**. The reason for this might be a shift of the equilibrium due to the better solubility of the monoradical compared to the diradical. Contrary to this result, it was not possible - even with an excess of antimony pentachloride - to get the dication of **6a**. The resulting salt always had a stoichiometry trithiole/SbCl$_6^-$ of 1:1.3. A trication of the tris-trithiole **9** could not be synthesized.

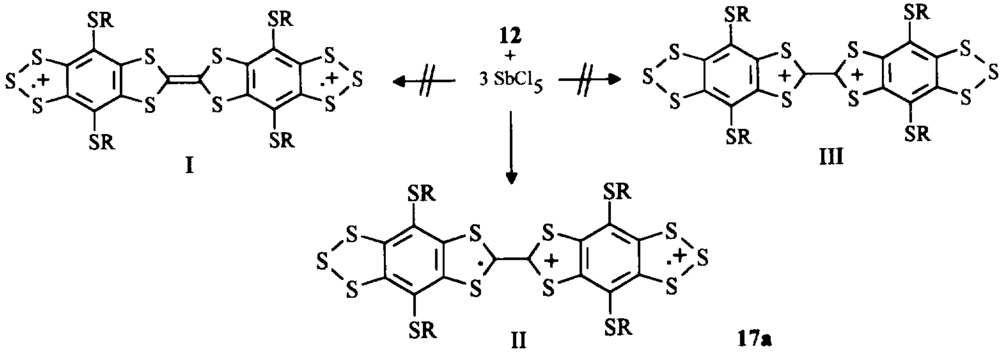


16d **16e** **16f**

R = -CH$_2$CH$_2$CH(CH$_3$)$_2$ R = -CH$_3$

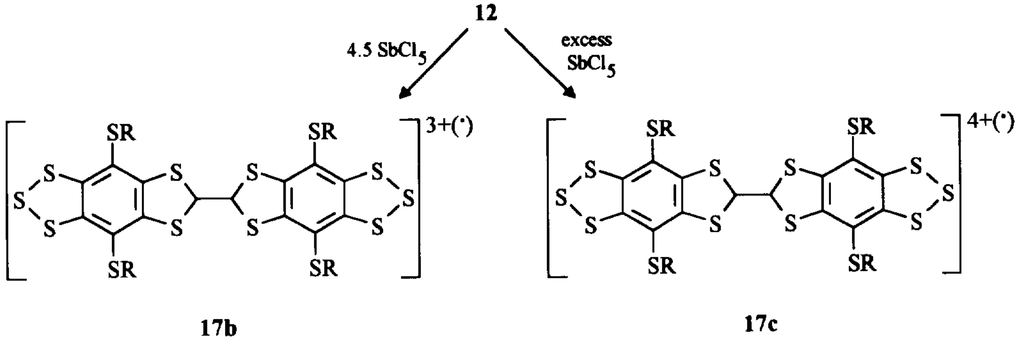
Scheme 6

Also the TTF-trithiole **12** yielded higher oxidized salts with an increasing amount of SbCl$_5$. Two equivalents of this oxidant afforded the dihexachloroantimonate **17a**. There are three possible structures for this product depending on the difference of the oxidation potentials of the trithiole groups and the TTF unit. The bis-trithiolium diradical (I) should be improbable, because the first oxidation potentials of perthio substituted dibenzo TTF are in the range of $0.6\ V < E^1_{1/2} > 0.8\ V$ [12] and this is about 0.4 V lower than the value for the comparable trithiole **3a** (wide supra). The first eliminated electron has to be a "TTF-electron". The EPR investigation of compound **17a** proved that **17a** was a radical species. Moreover a spin concentration of 2 spins per molecule was found. Based on these results, the bistrithiole-TTF radical dication **17a** should possess structure (II).



Scheme 7

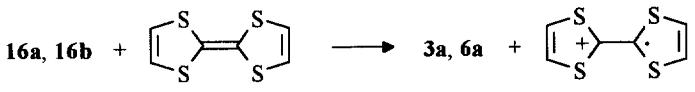
With 3 equivalents of antimony pentachloride the trihexachloroantimonate **17b** was formed. A mono- or a triradical are possible. Furthermore, an excess of antimony pentachloride yielded the fourfold charged molecule **17c**. The elucidation of the structure of **17b** and **17c** is still under investigation.



Scheme 8

Properties

The trithiolium radicals are stable if they are stored in a dry atmosphere. 4,5,6,7-Tetra(methylthio)benzo-1,2,3-trithiolium hexachloroantimonate **16a** shows no transformation after weeks. Compounds **16c**, **f** and **17** decompose after a few minutes on wet air. The radical cations were characterized by elemental analysis, UV-Vis-NIR- and EPR spectroscopy and by reduction with TTF to the starting trithiole. The UV-Vis-NIR spectra of the trithiolium hexachloroantimonates display a broad absorption from 1000 - 1500 nm in 1,2-dichloroethane. In its mass spectrum **16a** shows an M$^+$ peak of the parent trithiole with 100% intensity.



Scheme 9

As far as we know **16** and **17** are the first benzotrithiolium radical cations [13]. All trithiolium salts gave strong EPR signals. The radicals **16a**, **b**, **e** and **17a-c** show anisotropic spectra (for g-values *see* Experimental Part). The electrical conductivity was measured on pressed pellets (pressure: 20 kg cm^{-1}) indicating that the samples are in the range of semi-conductors. The details of the EPR spectroscopy and investigations concerning the magnetical behavior will be presented elsewhere.

Table 1: Electrical Conductivity of Trithiolium Salts

	16a	**16b**	**16c**	**16e**	**16f**	**17a**	**17b**	**17c**
σ [$S \cdot cm^{-1}$]	$2.7 \cdot 10^{-6}$	$4.4 \cdot 10^{-6}$	$9.3 \cdot 10^{-7}$	$9.6 \cdot 10^{-4}$	$6.3 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$4.5 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$

Experimental

For the preparation of compounds **3a,d** and **14** see [3].

4,5;6,7-Bis(ethylenedithio)benzo[1,2-d]1,2,3-trithiole (**3b**)

4,5;6,7-Bis(ethylenedithio)-1,3-dithiole-2-one [3] (300 mg, 0.86 mmol) was refluxed under nitrogen in a solution of sodium-*tert*-pentoxide (188 mg; 1.71 mmol) in 15 ml of methoxyethanol for 1 h. After cooling to room temperature SCl_2 (0.06 ml; 0.9 mmol) was added and the resulting precipitate was filtered off, washed with water, methanol and purified by silica gel column chromatography.

Eluent: chloroform; yield: 40%; mp. 195-197°C (toluene); calc. for $C_{10}H_8S_7$ (352.59): C 34.06, H 2.29, S 63.65; found: C 32.96, H 2.56, S 64.94; EI-MS m/z: 352 (100%, M^+), 324 (32%), 296 (30%); IR: ν [cm^{-1}] = 2910, 1411, 1276, 1120; UV-Vis (dichloroethane): λ_{max} [nm] = 309 (lg ε 4.25)

4,8-Bis(methylthio)benzo-1,2,3,5,7-pentathia-s-indacene-6-thione (**3c**)

The zinc(II)complex **2c** [3] (310 mg; 0.309 mmol) in 20 ml of anhydrous acetonitrile was treated with SCl_2 (0.2 ml; 0.309 mmol) in 10 ml of acetonitrile. The mixture was heated (50°C) for 1 h. After cooling to room temperature the resulting precipitate was filterd off, washed with water, methanol and purified by silica gel column chromatography.

Eluent: chloroform; yield: 67% ; mp. 193-195°C; calc. for $C_9H_6S_8$ (370.63): C 29.17, H 1.63, S 69.20; found: C 29.16, H 2.07, S 69.12; EI-MS m/z: 370 (100%, M^+), 358 (25%), 340 (20%), 322 (25%); IR: ν [cm^{-1}] = 1058; UV-Vis (dichloroethane): λ_{max} [nm] = 306 (lg ε 4.23), 391 (lg ε 4.28)

4,8-Bis(iso-pentylthio)benzo-1,2,3,5,7-pentathia-s-indacene-6-thione (**3e**)

Preparation analogous to the synthesis of **3b** starting from 4,8-bis(*iso*-pentylthio)benzo-1,3,5,7-tetrathia-s-indacene-2,6-thione [4c] (494 mg; 1 mmol) and NaOH (300 mg; instead of Na-*tert*-pentoxide).

Eluent: carbon tetrachloride; yield: 70%; mp. 72°C; calc. for $C_{17}H_{22}S_8$ (482.84): C 42.29, H 4.59, S 53.12; found: C 42.48, H 4.80, S 51.58; EI-MS m/z: 482 (100%, M^+), 412 (20%), 342 (20%); IR: ν [cm^{-1}] = 2950, 1070; UV-Vis (dichloroethane): λ_{max} [nm] = 394 (lg ε 4.22), 308 (lg ε 4.10)

7,8-Bis(iso-pentylthio)benzo-1,2,3,4,6-pentathia-as-indacene-5-one (**3f**)

Preparation analogous to the synthesis of **3b** starting from 7,8-bis(*iso*-pentylthio)-1,3,4,6-tetrathia-as-indacene-2,5-dione [14]. Yield: 61% ; mp. 47-52°C (the obtained oil crystallizes slow); calc. for $C_{17}H_{22}S_7O$ (466.78): C 43.74, H 4.75, S 48.08; found: C 43.31, H 5.51, S 47.33; EI-MS m/z: 466 (100%, M^+), 396 (28%), 366 (17%); IR: ν [cm^{-1}] = 1643; UV-Vis (dichloroethane): λ_{max} [nm] = 305 (lg ε 3.69); ^{1}H-NMR δ [ppm] ($CDCl_3$): 3.13 (t,2H), 2.95(t,2H), 1.70(m,2H), 1.49(q,4H), 0.89(d,12H); ^{13}C-NMR δ [ppm] ($CDCl_3$): 191.8, 154.8, 150.6, 141.7, 140.5, 132.7, 126.4, 38.5, 38.4, 35.5, 35.3, 27.46, 27.42, 22.2

Preparation procedure for bis(alkylthio)benzo-bis-1,2,3-trithioles **6** and **7**

The corresponding bis(alkylthio)benzo-tetrathiaindacene-2,6-diones **4** and **5** [4a] (1 mmol) were treated in 30 ml of THF at -10°C with six moles of methyllithium. The solutions were allowed to warm up to room temperature, and then stirred for 1 h. The trithioles were furnished by addition of SCl_2 (0.13 ml; 2 mmol) in 5 ml of anhydrous acetonitrile, stirring for another hour, filtering off (**7**: precipitating with methanol) and washing with water and methanol. Subjecting the crude product to column chromatography (silica gel) gave compounds **6** and **7**. As by-products **3d**, **f** were isolated.

4,8-Bis(methylthio)benzo[1,2-d][4,5-d']-bis-1,2,3-trithiole (**6a**)
Eluent: carbon tetrachloride; yield: 75%; mp. 208-210°C; calc. for $C_8H_6S_8$ (358.62): C 26.79, H 1.69; found: C 26.29, H 2.40; EI-MS m/z: 358 (30%, M^+); IR: ν [cm^{-1}] = 1409, 1250, 797; UV-Vis (dichloroethane): λ_{max} [nm] = 312 (lg ε 3.92)

4,8-Bis(iso-pentylthio)benzo[1,2-d][4,5-d']-bis-1,2,3-trithiole (**6b**)
Eluent: chloroform; yield: 81%; oil; calc. for $C_{16}H_{22}S_8$ (470.83): C 40.82, H 4.71, S 54.47; found: C 40.62, H 5.27, S 54.63; EI-MS m/z: 470 (100%, M^+), 438 (5%), 400 (15%), 330 (10%); IR: ν [cm^{-1}] = 2962, 1037; UV-Vis (dichloroethane): λ_{max} [nm] = 315 (lg ε 4.08); ^{1}H-NMR δ [ppm] ($CDCl_3$): 3.03 (t,4H), 1.73 (m,2H), 1.54 (q,4H), 0.91 (d,12H)

7,8-Bis(iso-pentylthio)benzo[1,2-d][3,4-d']-bis-1,2,3-trithiole (**7**)
Eluent: chloroform; yield: 43%; oil; calc. for $C_{16}H_{22}S_8$ (470.83): C 40.82, H 4.71, S 54.47; found: C 40.66, H 4.90, S 53.39; EI-MS m/z: 470 (40%, M^+), 400 (10%), 256 (100%); IR: ν [cm^{-1}] = 2960, 1029; UV-Vis (dichloroethane): λ_{max} [nm] = 316 (lg ε 4.0); ^{1}H-NMR δ [ppm] ($CDCl_3$): 2.99 (t,4H), 1.69 (m,2H), 1.50 (q,4H), 0.89 (d,12H); ^{13}C-NMR δ [ppm] ($CDCl_3$): 151.4, 134.5, 133.4, 38.3, 35.9, 27.5, 22.2

Benzo[1,2-d][3,4-d'][5,6-d'']-tris-1,2,3-trithiole (**9**)
Hexamercaptobenzene **8** (405 mg; 1.5 mmol) was deprotonated in 15 ml of THF at -10°C with **9** moles of methyllithium. After stirring for 30 min without cooling the resulting white suspension was added dropwise to a solution of sulfur dichloride (0.3 ml; 4.5 mmol) in 15 ml of THF at 0°C. The mixture was stirred for 1 h at room temperature. The orange precipitate was filtered off, washed with water, methanol, ether, chloroform and extracted several times with carbon disulfide. The unsoluble product was dried in vacuo.
Yield: 74%; mp. 195-200°C (decomposition); calc. for C_6S_9 (360.61): C 19.89, S 80.02; found: C 19.70, S 77.88 [15]; EI-MS m/z: 360 (18%, M^+), 296 (20%), 256 (55%), 160 (100%); IR: ν [cm^{-1}] = 1277, 1227 (very weak bands)

Benzo[3,4-d][5,6-d']-bis-1,2,3-trithiolo-[1,2-d'']pentathiepin (**10**)
The carbon disulfide filtrate of **9** afforded after removal of the solvent the orange compound **10**.
Yield: 20%; mp. 98-102°C (decomposition); calc. for C_6S_{11} (424.73): C 16.97, S 83.03; found: C 16.50, S 78.95 [15]; EI-MS m/z: 424 (1%, M^+), 360 (3%), 296 (3%), 256 (5%), 76 (100%); IR: ν [cm^{-1}] = 1502, 1274 (weak), 1223 (weak)

4,4',8,8'-Tetrakis(iso-pentylthio)-2,2'-bi-1,3,5,6,7-pentathia-s-indacenylidene (**12**)
Preparation analogous to the synthesis of **6** and **7** starting with the TTF **11** [4a]. After column chromatographic purification (silica gel) the product was recrystallized from toluene/*n*-butanol (2:3).
Eluent: carbon tetrachloride; yield: 73%; mp. 266-268°C; calc. for $C_{34}H_{44}S_{14}$ (901.56): C 45.30, H 4.92, S 49.78; found: C 45.30, H 5.68, S 48.40; EI-MS m/z: 900 (30%, M^+), 482 (100%), 412 (45%), 342 (40%); IR: ν [cm^{-1}] = 2954, 1240; UV-Vis (dichloroethane): λ_{max} [nm] = 314 (lg ε 4.67), 422 (lg ε 4.16); ^{1}H-NMR δ [ppm] ($CDCl_3$): 3.00 (t,8H), 1.75 (m,4H), 1.55 (q,8H), 0.93 (d,24H); ^{13}C-NMR δ [ppm] ($CDCl_3$): 147.5, 143.8, 122.7, 122.7, 38.7, 33.7, 27.3, 22.2

Preparation of **14** from **3** and NaCN

To a solution of **3** (1 mmol) in 35 ml of acetonitrile NaCN (49 mg; 1 mmol) was added. After stirring colorless precipitates of the tetrathiocines were filtered off and purified [3].

Bis(1,2,3,4-tetrakis(methylthio)benzo)[c,g]1,2,5,6-tetrathiocine (**14a**)
Reaction time: 30 min; yield: 95%; mp. 260°C, lit.[3]: 261°C

Bis(4,7-bis(isopentylthio)benzo-1,3-dithiole-2-thione)[c,d]1,2,5,6-tetrathiocine (**14e**)
Reaction time: 20 h; yield: 92%; mp. 248°C, lit.[3]: 246-248°C

Pentakis(methylthio)benzothiocyanate (**15a**)
Compound **14a** (650 mg; 1mmol) was suspended under inert gas conditions in 30 ml of DMF and treated with NaCN (98 mg; 2 mmol). After stirring for 8 h methyl iodide (0.18 ml; 3 mmol) was added. 20 min later the solvent was removed from the yellow solution. Subjecting the resulting material to column chromatography (silica gel) and recrystallization from ethanol afforded **15a**.
Eluent: carbon tetrachloride; yield: 31%; mp. 65-66°C; calc. for $C_{12}H_{15}S_6N$ (365.62): C 39.42, H 4.14, S 52.61, N 3.83; found: C 40.15, H 4.73, S 51.86, N 3.58; EI-MS m/z: 365 (70%, M^+), 324 (100%); IR: ν [cm^{-1}] = 2910, 2144; ^{1}H-NMR δ [ppm] ($CDCl_3$): 2.54 (s,6H), 2.51 (s,9H); ^{13}C-NMR δ [ppm] ($CDCl_3$): = 150.6, 149.5, 145.3, 137.5, 111.2, 21.1, 21.0, 20.9

Preparation procedure for the trithiolium radical cations **16** and the TTF-trithiolium radical cations **17**

The corresponding trithioles **3** or **6** or the TTF-trithiole **12** (0.5 mmol) were treated in 20 ml of 1,2-dichloroethane under anhydrous conditions with a solution of $SbCl_5$ (1 ml) in 10 ml of dichloroethane.

4,5,6,7-Tetrakis(methylthio)benzo[1,2-d]1,2,3-trithiolium hexachloroantimonate (**16a**)
Amount of $SbCl_5$ solution: 1 ml; reaction time: 30 min; purification: filtering off and washing with dichloroethane; yield: 97%; mp. 149°C (decomposition); calc. for $C_{10}H_{12}S_7Cl_6Sb$ (691.09): C 17.38, H 1.75, S 32.47, Cl 30.78; found: C 17.49, H 2.18, S 32.20, Cl 30.70; EI-MS m/z: 356 (100%, M^+), 326 (20%), 308 (55%), 296 (32%); IR: ν [cm^{-1}] = 2919, 1469, 1413, 1300, 1120, 974, 473; UV-Vis (dichloroethane): λ_{max} [nm] = 830 (lg ε 3.22); spin concentration in spins per molecule: 1

g-values: temperature	g_{xx}	g_{yy}	g_{zz}	<g>
20°C	2.02605	2.02176	2.00355	2.01565
-150°C	2.02461	2.02185	2.00280	2.01497

4.8-Bis(methylthio)benzo[1,2-d]1,2,3-trithiolo[4,5-d']1,2,3-trithiolium hexachloroantimonate (**16b**)
Amount of $SbCl_5$ solution: 1 ml; reaction time: 30 min; purification: filtering off and washing with dichloroethane; yield: 92%; calc. for $C_8H_6S_8Cl_6Sb$ (693.08): C 13.86, H 0.87, S 37.01, Cl 30.69; found: C 14.43, H 1.09, S 36.11, Cl 31.30; UV-Vis (dichloroethane): λ_{max} [nm] = 1150 (lg ε 3.5), 1420 (lg ε 3.4) (very broad absorption bands); spin concentration in spins per molecule: 1

g-values: temperature	g_{xx}	g_{yy}	g_{zz}	<g>
20°C	2.02454	2.01579	2.00303	2.01445
-150°C	2.02080	2.01230	2.00245	2.01185

Benzo[3,4-d][5,6-d']bis-1,2,3-trithiolo-[1,2-d"]1,2,3-trithiolium hexachloroantimonate (**16c**)
Amount of $SbCl_5$ solution: 1.8 ml; reaction time: 40 min; purification: filtering off and washing with dichloroethane; yield: 83%; calc. for $C_6S_9Cl_6Sb$ (695.07): C 10.37, S 41.51; found: C 11.10, S 39.15; g-value: 2.01578

4.8-Bis(iso-pentylthio)benzo [1,2-d][4,5-d']bis-1,2,3-trithiolium di(hexachloroantimonate) (**16d**)
Amount of $SbCl_5$ solution: 2 ml; reaction time: 30 min; purification: filtering off and washing with *n*-hexane; yield: 87%; calc. for $C_{16}H_{22}S_8Cl_{12}Sb_2$ (1139.77): C 16.86, H 1.95, S 22.50, Cl 37.33; found: C 17.15, H 2.50, S 22.49, Cl 35.77; UV-Vis (dichloroethane): λ_{max} [nm] = 1160 (very broad band: 950-1500); g-value: 2.0170

4.8-Bis(methylthio)benzo[1,2-d][4,5-d']bis-1,2,3-trithiolium di(hexachloroantimonate) (**16e**)
Amount of $SbCl_5$ solution: 4 ml; reaction time: 60 min; purification: filtering off and washing with dichloroethane; yield: 84%; calc. for $C_8H_6S_8(SbCl_6)_{1.3}$ (793.43): C 12.10, H 0.76, S 32.32; found: C 12.14, H 1.34, S 31.21; UV-Vis (dichloroethane): λ_{max} [nm] = 1215 (lg ε 3.89), 1444 (lg ε 3.83); g-value (<g>): 2.0220

Benzo[1,2-d]1,2,3-trithiolo-[3,4-d'][5,6-d'']bis-1,2,3-trithiolium di(hexachloroantimonate) **(16f)**
Amount of $SbCl_5$ solution: 7 ml; reaction time: 50 min; purification: filtering off and washing with dichloroethane; yield: 94%; calc. for $C_6S_9Cl_{12}Sb$ (1029.54): C 7.00, S 28.03; found: C 8.41, S 28.48; g-value: 2.01530

4,4',8,8'-Tetrakis(iso-pentylthio)-2,2'-bi-1,3,5,6,7-pentathia-s-indacenylidenium di(hexachloroantimonate) **(17a)**
Amount of $SbCl_5$ solution: 2 ml; reaction time: 30 min; purification: removal of 70% of the solvent and addition of 10 ml of *n*-hexane, washing with *n*-hexane; yield: 79%; calc. for $C_{34}H_{44}S_{14}Cl_{12}Sb_2$ (1570.50): C 26.00, H 2.82, S 28.58; found: C 26.29, H 3.46, S 27.47; UV-Vis (dichloroethane): λ_{max} [nm] = 1400, 1170 (very broad absorption bands), 458

g-values: temperature	g_{xx}	g_{yy}	g_{zz}	<g>
20°C	2.03010	2.02163	2.00371	2.01848
-150°C	2.02977	2.02129	2.00278	2.01795

4,4',8,8'-Tetrakis(iso-pentylthio)-2,2'-bi-1,3,5,6,7-pentathia-s-indacenylidenium tri(hexachloroantimonate) **(17b)**
Amount of $SbCl_5$ solution: 3 ml; reaction time: 50 min; purification: removal of 30% of the solvent, addition of 10 ml of *n*-hexane, filtering off and washing with *n*-hexane; yield: 92%; calc. for $C_{34}H_{44}S_{14}Cl_{18}Sb_3$ (1904.97): C 21.43, H 2.31, S 23.53, Cl 33.56; found: C 21.94, H 2.75, S 23.82, Cl 31.95; UV-Vis (dichloroethane): λ_{max} [nm] = 1400, 1245 (very broad absorption bands), 462

g-values: temperature	g_{xx}	g_{yy}	g_{zz}	<g>
20°C	2.03033	2.02182	2.00349	2.01855
-150°C	2.02932	2.02090	2.00245	2.01756

4,4',8,8'-Tetrakis(iso-pentylthio)-2,2'-bi-1,3,5,6,7-pentathia-s-indacenylidenium tetra(hexachloroantimonate) **(17c)**
Amount of $SbCl_5$ solution: 9 ml; reaction time: 50 min; purification: filtering off and washing with *n*-hexane; yield: 89%; calc. for $C_{34}H_{44}S_{14}Cl_{24}Sb_4$ (2239.44): C 18.23, H 1.96, S 20.01, Cl 38.07; found: C 18.24, H 2.76, S 18.91, Cl 36.29; UV-Vis (dichloroethane): λ_{max} [nm] = 1385, 1220 (very broad absorption bands), 456

g-values: temperature	g_{xx}	g_{yy}	g_{zz}	<g>
20°C	2.02777	2.01997	2.00338	2.01704
-150°C	2.02693	2.01925	2.00263	2.01627

Reduction of trithiolium radicals with tetrathiafulvalene

The radicals **16a** and **16b** (0.3 mmol) were treated in 20 ml of dichloroethane with tetrathiafulvalene (80 mg, 0.3 mmol). After stirring for 45 min and removal of the solvent, the residue was extracted with ether. The products **3a** and **6a** in the ethereal layers were subjected to column chromatography (silica gel, carbon tetrachloride).

Tetrakis(methylthio)benzo-1,2,3-trithiole **(3a)**
yield: 89%; mp. 90°C, lit.[3]: 91°C

4,8-Bis(methylthio)benzo[1,2-d][4,5-d']bis-1,2,3-trithiole **(6a)**
yield: 79%; mp. 208-210°C

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15. In the microanalysis difficulties occurred to determine exact sulfur values higher than 50% due to the device configuration.

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