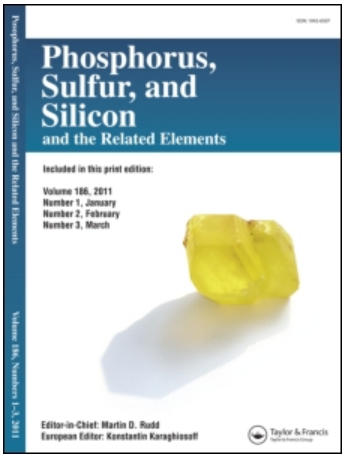

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ORGANOMETALLOIDAL COMPOUNDS WITH *O*-PHENYLENESUBSTITUENTS, PART XXVII.[1] SYNTHESIS, CHARACTERIZATION AND STRUCTURE DETERMINATION OF 2,3,7,8-TETRAKIS(METHYLTHIO)-AND 2,3;7,8-BIS(ETHYLENEDITHIO)THIANTHRENE

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ORGANOMETALLOIDAL COMPOUNDS WITH *o*-PHENYLENESUBSTITUENTS, PART XXVII.[1] SYNTHESIS, CHARACTERIZATION AND STRUCTURE DETERMINATION OF 2,3,7,8-TETRAKIS(METHYLTHIO)- AND 2,3;7,8-BIS(ETHYLENEDITHIO)THIANTHRENE

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A generally applicable synthesis via the sequence thiophenol (**3**), 1,2-bis(alkylthio)benzene (**6**), 1-bromo-3,4-bis(alkylthio)benzene (**7**), bis[3,4-bis(alkylthio)phenyl]sulfide (**8**), bis[2-bromo-4,5-bis(alkylthio)-phenyl]sulfide (**9**), 2,3,7,8-tetrakis(alkylthio)thianthrene (**2**) has been worked out for the title compounds. Their ^{1}H-NMR, MS and CV data are given, the results of the crystal structure determinations as well.

Key words: 2,3,7,8-tetrakis(alkylthio)thianthrenes; synthesis; 2,3,7,8-tetrakis(methylthio)- and 2,3;7,8-bis(ethylendithio)thianthrene; ^{1}H-NMR; MS; CV data; X-ray structures.

1. INTRODUCTION

Electron-rich chalcogenanthrenes such as 2,3,7,8-tetramethoxythianthrene (**1**) can be oxidized to their monocations; the resulting compounds possess colomnar structures with segregated stacks of cations and anions.[2] Using 7,7,8,8-tetracyanoquinodimethane or tetracyanoethene as acceptors charge transfer complexes are formed, again with columnar structures, however with stacks in which the donor and acceptor molecules alternate.[3,4] All these compounds show only poor electrical conductivities and behave as semiconductors. Better electrical conductivities may be expected for derivatives of the corresponding tetrakis(alkylthio)-chalcogenanthrenes since for organic metals on the base of tetrathiafulvalenes[5] the introduction of organylthio substituents even led to superconduction.[6]

We therefore are interested in the hitherto unknown 2,3,7,8-tetrakis(alkylthio)-thianthrenes (**2**) as potential starting materials for organic metals. This paper is concerned with the synthesis and characterization of the tetrakis(alkylthio)thianthrenes (**2**) themselves in comparison with the corresponding tetrakis(alkoxy) derivatives (**1**).

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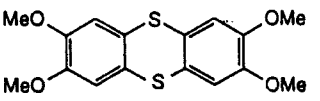

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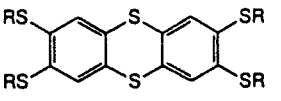
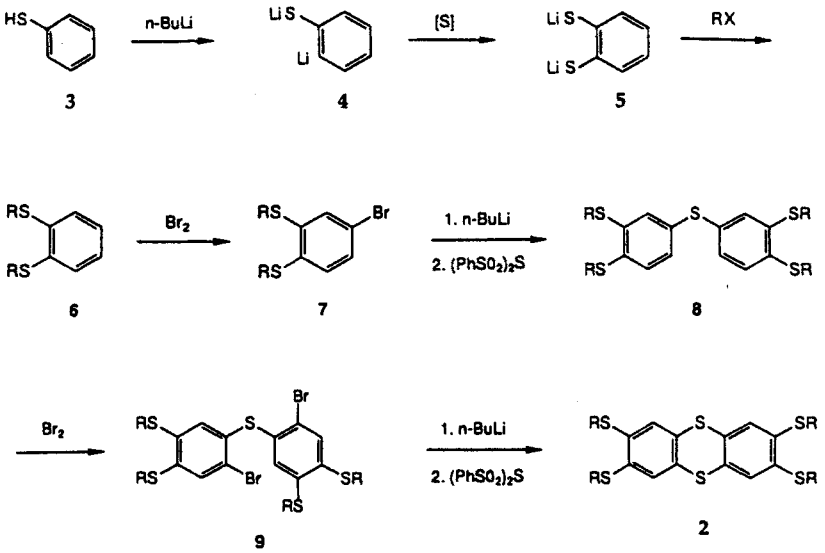


2 a (R = CH_3)
b (R = 1/2 CH_2CH_2)

2. PREPARATION OF TETRAKIS(ALKYLTHIO)THIANTHRENES

In a short communication[7] a synthesis for 2,3,7,8-tetrakis(methylthio)thianthrene (**2a**) has been described. Meanwhile each step was optimized and a generally applicable method for 2,3,7,8-tetrakis(alkylthio)thianthrenes worked out (Scheme I). The first steps (**3** → **4** → **5**) follow procedures already reported in the literature.[8–12] For **5a** dimethylsulfate, for **5b** 1,2-dibromoethane was used as an alkylating agent. Bis(diphenylsulfinyl)sulfide proved to be better than sulfurdichloride as sulfur(II)-component for the preparation of **8** and **2**, respectively.



SCHEME I

3. CHARACTERIZATION OF COMPOUNDS

^{1}H-NMR Spectra

The data for the hitherto unknown compounds **7–9** and **2** are given in Table I. Except for the methyl and methylene protons of the alkylthio substituents the protons at the aryl rings show no significantly different chemical shifts for the methylthio or ethylenedithio series. All the values lie in the normal ranges. In compounds **7–9** the two alkylthio substituents are chemically nonequivalent. In the case of the methylthio series two signals for the methyl protons are seen in the spectra, but no assignment was made since it was not necessary as a proof of the

TABLE I

^{1}H-NMR data of thianthrenes **2** and of their intermediates **7–9** (BRUKER WP 250, AM 360, WM 400 resp.)

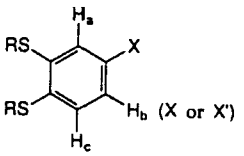
compound	measuring frequency [MHz]	solvent	chemical shifts [ppm][a] (TMS as standard)					coupling constants[b] [Hz]	
			H_a	H_b	H_c	$-SCH_3$, $-SCH_2-$ resp.		$J(H_aH_b)$	$J(H_bH_c)$
7a	400	$CDCl_3$	7.24	7.22	7.04	2.46[c]	2.42[c]	2.1	8.2
7b	250	CD_2Cl_2	7.29	7.07	6.98	3.22		2.0	8.3
8a	360	CD_2Cl_2	7.15	7.08	7.11	2.44[c]	2.39[c]	1.8	8.1
8b	250	$CDCl_3$	7.14	6.95	7.07	3.25		2.1	8.2
9a	250	$CDCl_3$	6.96[d]	-	7.38[d]	2.46[c]	2.32[c]	-	-
9b	250	$CDCl_3$	6.95[d]	-	7.42[d]	3.26		-	-
2a	250	$CDCl_3$	7.28	-	= H_a	2.46		-	-
2b	250	$CDCl_3$	7.27	-	= H_a	3.26		-	-

[a] assignment according to the opposite illustration

[b] para coupling not observed

[c] no assignment made

[d] assigment based on increments



structure; in the ethylenedithio series only broad, not resolvable signals are obtained for the ethylene protons.

MS Data

The results of mass spectroscopic investigations obtained for the thianthrenes **2a** and **2b** are compiled in Table II. For both compounds the peaks of highest intensity are the molecule peaks M^+, indicating that the compounds can easily be oxidized. This is also documented by the M^{2+} peaks in the spectra.

In the case of the methylthio compound **2a** different fragmentation paths are observed: (1) fragmentation of the central dithiin ring forming the aromatic dibenzothiophen derivative by extrusion of a sulfur atom, and (2) fragmentation of two ortho-standing methylthio substituents by elimination of (a) methane to a methylenedithio group which can be dehydrogenated to the corresponding aromatic dithiolium compound, or (b) CH_3, CH_2S and/or S leading to thiacyclopropene derivatives or protonated forms of them.

In contrast, the ethylenedithio groups of **2b** are much more labile: preferably ethene and sulfur are eliminated and the corresponding thiacyclopropene derivatives formed.

CV Measurements

Due to solubility problems, the cyclovoltammetric measurements had to be carried out in dichloromethane as a solvent, in which the measuring range is reduced since

TABLE II

MS data of the thianthrenes **2** (Finnegan MAT CH7, 70 eV)

2a			**2b**		
mass	intensity [%]	fragment	mass	intensity [%]	fragment
400	100.0	M^+	396	100.0	M^+
352	6.1	$M^+ - S, - CH_4$	394	11.0	$M^+ - H_2$
320	5.6	$M^+ - 2S, - CH_4$	336	11.0	$M^+ - C_2H_4, - S$
307	5.3	$M^+ - S, - CH_3, -CH_2S$	276	7.5	$M^+ - 2C_2H_4, - 2S$
306	10.4	$M^+ - S, - 2CH_3, - S$	198	6.4	M^{2+}
291	7.6	$M^+ - S, - CH_4, - CH_3, - CH_2S$			
290	7.3	$M^+ - S, - CH_4, - 2CH_3, - S$			
289	25.8	$M^+ - S, - CH_4, - H, - 2CH_3, - S$			
259	9.3	$M^+ - 2S, - CH_4, - CH_3, - CH_2S$			
200	5.6	M^{2+}			

TABLE III

CV data of **2a** and **2b**, CH_2Cl_2 as solvent, SCE as reference

	2a				**2b**
V [mV/s]	E_a^1 [mV]	E_k^1 [mV]	E_a^2 [mV]	E_k^2 [mV]	E_a^1 [mV]
20	1065	990	1355	1275	1070
50	1060	985	1350	1275	1080
100	1070	985	1350	1270	1110
200	1070	985	1350	1260	1130

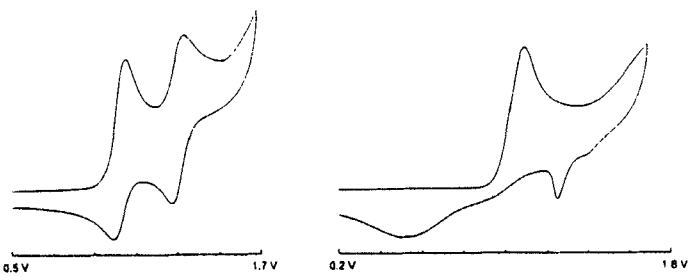


FIGURE 1 Cyclovoltammograms of **2a** (left) and **2b** (right).

at 1.7 V (referred to the standard calomel electrode) the solvent itself showed reaction. Only the methyldithio derivative **2a** exhibited reversible behaviour with two oxidation and reduction peaks, the peak/current ratio of 1 indicating a one electron transfer in each step. The ethylenedithio compound **2b** shows an irreversible behaviour with only one oxidation peak (Table III, Figure 1).

A comparison of the halfwave potentials $E_{1/2} = (E_a + E_k)/2$ of the tetrakis(methylthio)-compound **2a** ($E^1_{1/2}$ = 1030 mV, $E^2_{1/2}$ = 1315 mV) and of the corresponding tetramethoxy compound **1** ($E^1_{1/2}$ = 980 mV, $E^2_{1/2}$ = 1370 mV)[13] shows the first oxidation potential to be higher for **2a**, the second, however, for **1**. This is probably due to two oppositely directed effects, i.e. methylthio groups stabilize cations less than methoxy groups, but are more easily oxidized.

4. CRYSTAL STRUCTURE DETERMINATIONS

The crystal structures of the thianthrenes **2a** and **2b** were determined. Suitable crystals were obtained by evaporating solutions of **2a** in trichloromethane and of **2b** in dichloromethane. The quality of the single crystals of **2a** were relatively bad, but good enough to get reliable information on the packing of the molecules in the crystal. The results are given in Tables IV–VI.

Molecular Structures

The molecules of **2a** and of **2b** are folded at their SS axes (Figure 2). The angles of fold (defined as the angles between the normals to the best planes through the phenyl rings of the molecule) are 129.7 and 124.9° resp. and lie in the range of 122–134° for thianthrene derivatives.[1b,14,15] Also the bond lengths and angles in

TABLE IV

Data collection and structure refinement parameters (e.s.d.'s in parentheses)

compound	**2a** $C_{16}H_{16}S_6$	**2b** $C_{16}H_{12}S_6$
M [g/mol]	400.7	396.6
crystal system	triclinic	triclinic
space group	P 1	P 1
a [pm]	573.8(5)	707.0(2)
b [pm]	1132.5(4)	1048.8(2)
c [pm]	1437.3(6)	1259.6(3)
α [°]	87.93(3)	66.50(2)
β [°]	88.04(5)	82.83(2)
γ [°]	80.90(5)	77.96(2)
V [10^6 pm^3]	921.3(9)	836.9(3)
Z	2	2
$d_{(calc)}$ [$g \cdot cm^{-3}$]	1.44	1.57
independent reflections	3456	3650
reflections with $\|F_0\| > n \cdot (\|F_0\|)$	1433 (n=6)	2408 (n=7)
refined parameters	204	207
absorption coefficient [cm^{-1}]	7.1	1.57
R; R_w	0.088; 0.074	0.066; 0.058

TABLE V

Refined atomic coordinates and equivalent isotropic thermal parameters (defined as one third of the trace of the orthogonalized μ_{ij} tensor) for **2a** and **2b** with e.s.d.'s in parentheses

		J = 1				J = 2			
	atom	x/a	y/b	z/c	Ueq	x/a	y/b	z/c	Ueq
2a	S(J)	0.0200(7)	0.1129(3)	0.8564(1)	0.047(1)	-0.3608(7)	0.0062(3)	0.7368(2)	0.051(1)
	S(J4)	0.0278(8)	-0.4500(3)	0.8595(2)	0.068(1)	-0.0757(8)	0.2585(3)	0.4257(2)	0.067(1)
	S(J5)	0.3649(8)	-0.3492(3)	0.9804(2)	0.065(1)	0.2649(8)	0.3682(3)	0.5408(2)	0.063(1)
	C(J1)	0.023(2)	-0.0438(9)	0.8549(7)	0.036(5)	-0.009(2)	0.149(1)	0.7341(7)	0.040(5)
	C(J2)	-0.148(2)	-0.089(1)	0.8045(7)	0.036(4)	-0.171(2)	0.1022(9)	0.6838(7)	0.041(5)
	C(J3)	-0.146(2)	-0.214(1)	0.8026(7)	0.044(5)	-0.198(2)	0.133(1)	0.5876(7)	0.046(5)
	C(J4)	0.015(2)	-0.290(1)	0.8581(7)	0.038(5)	-0.057(3)	0.215(1)	0.5470(7)	0.053(6)
	C(J5)	0.174(3)	-0.246(1)	0.9099(8)	0.045(5)	0.110(2)	0.265(1)	0.5985(8)	0.045(5)
	C(J6)	0.182(2)	-0.121(1)	0.9082(7)	0.044(5)	0.133(2)	0.2284(9)	0.6929(7)	0.041(5)
	C(J7)	-0.210(3)	-0.474(1)	0.7833(8)	0.072(7)	-0.286(3)	0.175(1)	0.3837(7)	0.061(5)
	C(J8)	0.554(3)	-0.262(1)	1.0326(8)	0.074(6)	0.436(2)	0.419(1)	0.6303(8)	0.062(6)
2b	S(J)	0.5577(2)	0.0751(1)	0.6183(1)	0.0458(4)	0.9484(2)	0.1512(1)	0.6603(1)	0.0473(4)
	S(J4)	0.6112(3)	0.2932(1)	1.0129(1)	0.0834(7)	1.3325(2)	-0.3711(1)	0.7093(1)	0.0614(5)
	S(J5)	0.2014(2)	0.1799(1)	0.9878(1)	0.0621(5)	0.9201(3)	-0.4386(1)	0.6435(1)	0.0748(6)
	C(J1)	0.5716(7)	0.1260(4)	0.7358(3)	0.037(1)	0.7789(7)	-0.0469(4)	0.6343(3)	0.035(1)
	C(J2)	0.7387(7)	0.1649(4)	0.7504(3)	0.037(1)	0.9471(7)	-0.0174(4)	0.6586(3)	0.036(1)
	C(J3)	0.7417(7)	0.2140(4)	0.8380(3)	0.042(1)	1.1133(7)	-0.1160(4)	0.6764(3)	0.040(1)
	C(J4)	0.5786(8)	0.2246(4)	0.9100(4)	0.044(1)	1.1157(7)	-0.2481(4)	0.6729(3)	0.040(1)
	C(J5)	0.4137(7)	0.1813(4)	0.8984(4)	0.042(1)	0.9475(8)	-0.2769(4)	0.6469(3)	0.039(1)
	C(J6)	0.4112(7)	0.1307(4)	0.8105(3)	0.040(1)	0.7811(7)	-0.1774(4)	0.6284(3)	0.040(1)
	C(J7)	0.396(1)	0.3007(8)	1.0894(6)	0.102(4)	1.321(1)	-0.4696(5)	0.6203(5)	0.075(2)
	C(J8)	0.215(1)	0.3225(6)	1.0334(5)	0.088(3)	1.149(1)	-0.5415(6)	0.6522(6)	0.090(3)

the central dithiin ring of both compounds correspond to the typical values in other thianthrenes[1b,14,15] (Table VI) and therefore need no further discussion. The arrangements of the alkylthio substituents deserve a closer look.

In **2a** the four methylthio groups are coplanar to the phenyl rings they belong to, all in *exo*-positions; an analogous situation is also found in the comparable 2,3,7,8-tetramethoxy-thianthrene (**1**).[15] Due to steric interactions between the methyl group and the *ortho*-standing hydrogen atom of the phenyl ring the angles CCS_{exo} are larger and the corresponding angles CCS_{endo} smaller than the ideal values of 120°. As expected, the distances SC_{alk} are somewhat longer than those of SC_{ar}.

In **2b**, however, the ethylenedithio group as part of a dihydrodithiin ring is no more planar: one of the $C_{ar}SC_{alk}$ groups is still coplanar to the plane of the phenyl ring, the other one carries out the rotation required, this behaviour can be understood by the crystal structure (see below, Figure 7). Due to this, the SC_{alk} distance of the coplanar CSC group is strikingly shortened, its $C_{ar}SC_{alk}$ angle enlarged in comparison with the rotated CSC group (Table VI). As a consequence of the cyclic

TABLE VI

Mean values of bond length [pm], bond angles [°] for **2a** and **2b** (e.s.d.'s in parentheses)

		2a	**2b**
thianthrene moiety	CS	179(1)	177.7(5)
	CC	141(1)	138.9(7)
	CSC	99.7(5)	99.3(2)
	CCS_{exo}	118.5(8)	119.8(4)
	CCS_{endo}	121.0(8)	120.5(3)
	CCC	120(1)	120.0(4)
	Ph_1/Ph_2	129.7	124.9
alkylthio substituents	$C_{ar}S$	178(1)	176.9(5); 176.1(5)
	$C_{alk}S$	180(1)	171.9(8); 182.1(7)
	$C_{alk}C_{ar}$	-	148(1)
	CSC	104.4(6)	106.7(4); 103.3(3)
	$C_{ar}C_{ar}S_{exo}$	122.4(9)	114.0(4); 116.2(4)
	$C_{ar}C_{ar}S_{endo}$	117.2(9)	126.0(4); 124.7(4)
	$C_{alk}C_{alk}S$	-	119.1(5); 112.7(5)
	$Ph/C_{ar}SC_{alk}$	-	4.4; 28.4

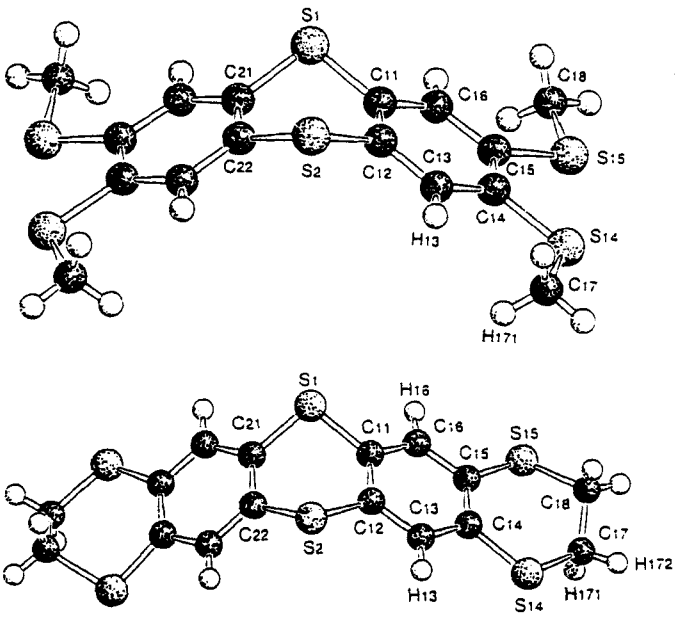


FIGURE 2 Molecular structures of **2a** (top) and **2b** (bottom) and numbering scheme of atoms.

structure, the angles CCS_{exo} are larger than the CCS_{endo} ones, thus differing from the situation in **2a**.

Crystal Structures

The unit cells of **2a** and **2b** are shown in Figure 3. Relative to the basic *ab* plane the SS axes of the molecules are inclined in the case of **2a** and perpendicular in the case of **2b**, leading to different packing modes in the crystal.

In **2a** a columnar structure is formed which remembers to that in the tetragonal form of 2,3,7,8-tetramethoxyselenanthrene (**10**)[16] (Figure 4). However, the relative arrangements of the stacks differ in the two compounds. As can be seen from the top views given in Figure 5, in **10** pairs of oppositely arranged selenanthrene

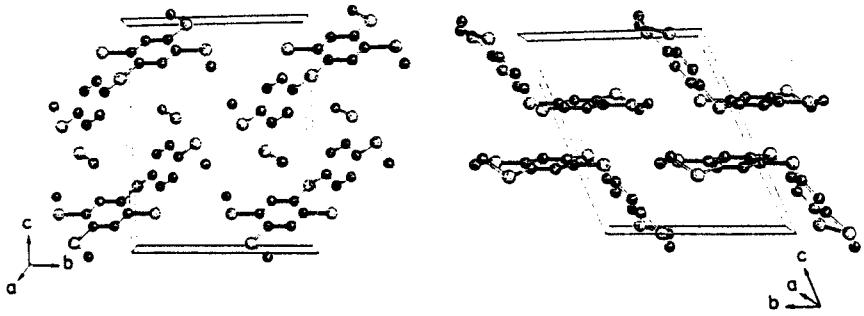


FIGURE 3 Unit cells of **2a** (left) and **2b** (right).

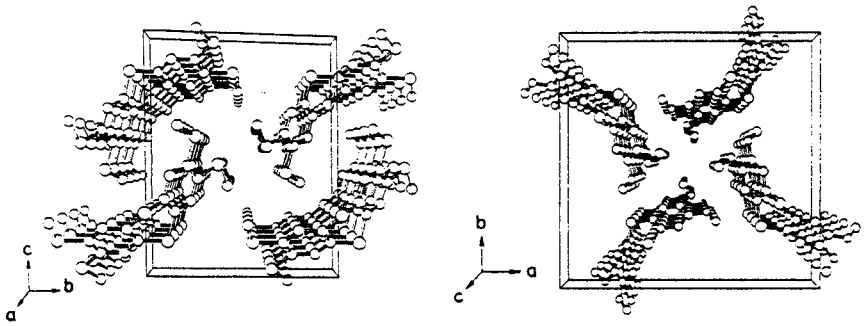


FIGURE 4 Stacks of molecules in the crystal of **2a** (left) and of **10** (right) for comparison.

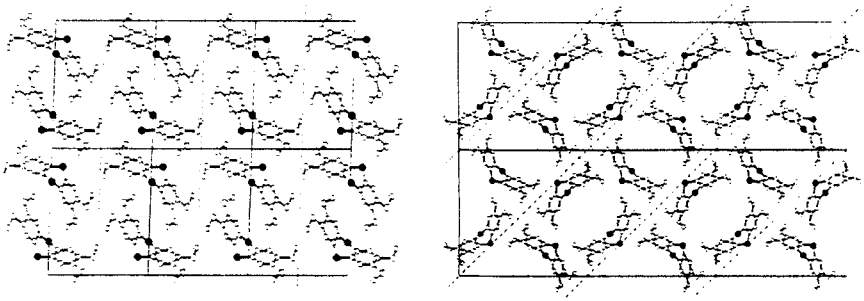


FIGURE 5 Chains formed by pairs of chalcogenanthrene molecules in the crystals of **2a** (left) and of **10** (right) for comparison.

molecules form linear chains in which the SeSe′ axes of subsequent pairs are alternately parallel and perpendicular to the chain direction. The arrangement of the selenanthrene molecules in these pairs corresponds to the orientation of the donor molecules in the 2:1 CT complexes of **10** with tetracyanoethene.[4] In **2a** also pairs of thianthrene molecules are found, still opposite to each other, however no more in front position, but slightly shifted in such a way that the two molecules interlock to some extent. Again chains are found, but now of uniformly aligned pairs. Thus, a closer packing is achieved in **2a** than in **10**, documented by the volumina of the unit cells: $921 \cdot 10^6$ pm^3 for **2a** (Z = 2) and $1999 \cdot 10^6$ pm^3 for **10** (Z = 4), i.e. one molecule of **2a** occupies a smaller volume than one of **10** although 6 S require more space than 2 Se + 4 O.

In the stacks of **2a** the SS axes of the molecules are inclined to the stacking axis (angle of inclination 49.8°, in the comparable stacks of **10** 41.4° are found). In the stacks the sulfur atoms of the central dithiin rings form a zigzag chain (Figure 6) in which the intramolecular distance (d_1 = 323 pm) is shorter, the intermolecular one (d_2 = 393 pm) longer than the van der Waals distance (370 pm[17]). Analogous chains are formed by the sulfur atoms of the peripheral methylthio groups. In **10** both distances (d_1 and d_2) are shorter than the corresponding van der Waals distance.

In the crystal of **2b** pairs of thianthrene molecules can be found, too. The two molecules are still more closely interlocked in **2b** than in **2a**, so that the planes of one half of each molecule are parallel to each other (Figure 7). Thus, the sulfur atoms of the dithiin moiety of one molecule and of the ethylendithio group of the other are brought relatively close together, however the shortest values of 457 and 492 pm are still significantly longer than the van der Waals distance.

In the projection of Figure 8 the uniformly arranged pairs of thianthrene molecules seem to form linear chains. However, in these chains subsequent pairs alternate in height, forming zigzag lines; the SS contacts between different pairs are 840–900 pm and therefore without significance.

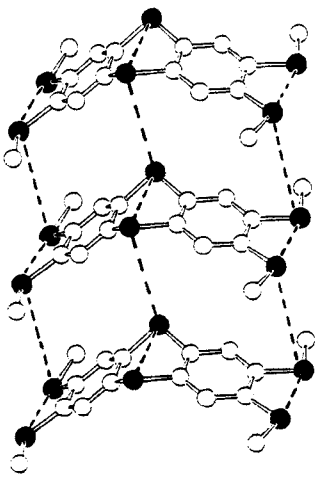


FIGURE 6 Sulfur/sulfur contacts in the stacks of thianthrene molecules in the crystal of **2a**.

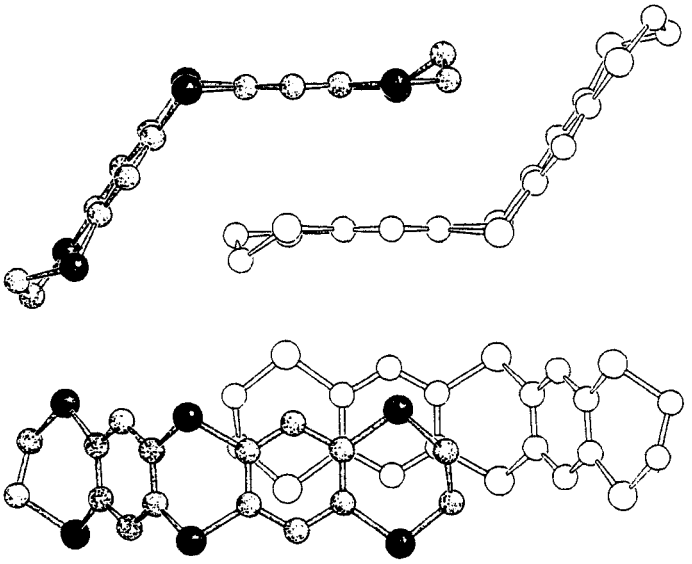


FIGURE 7 Top and side view of a pair of thianthrene molecules in the crystal of **2b**.

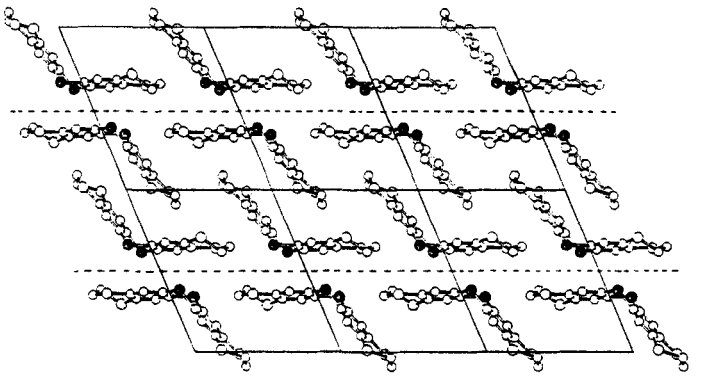


FIGURE 8 Arrangement of the pairs of thianthrene molecules in the crystal of **2b** (projection to the *bc* plane).

EXPERIMENTAL

All operations are performed under an atmosphere of dry nitrogen. The analyses data of the new compounds are listed in Table VII.

1,2-Bis(alkylthio)benzenes **6** *are obtained by alkylating the crude dilithium benzene-1,2-dithiolate* (**5**) *prepared by the following one pot procedure*: To the stirred mixture of 122 ml (0.8 mol) *N,N,N',N'*-tetramethyl-ethylenediamin (TMEDA) in 600 ml cyclohexane and 500 ml lithium *n*-butyl (1.6 M in *n*-hexane, 0.8 mol), cooled to 0°C, the solution of 42.2 ml (43.8 g, 0.4 mol) benzenethiol (thiophenol) in 75 ml cyclohexane is added dropwise. The reaction mixture is then stirred at room temperature for 24 h. A white suspension of **4** is formed to which with vigorous stirring 12.8 g (0.4 mol) powdered sulfur is added. After having been refluxed for 8 h the solvents are distilled off leaving **5** as a dark red brown residue. **6a** (R = CH_3): The above described residue, dissolved in 500 ml 10% aqueous sodium hydroxide, is methylated by 50 ml (66.5 g, 0.53 mol) dimethyl sulfate. Yield 44.0 g (64.6%), $bp_{2.5}$ 95–97°C (lit.:[18] bp_1 = 70–80°C), n_D^{20} 1.6420. **6b** (R = 1/2 CH_2CH_2). Alternatively, the solution of the residue in 500 ml ethanol is alkylated by 35 ml (76.3 g, 0.4 mol) 1,2-dibromoethane in 125 ml ethanol

TABLE VII
Analyses data of the new compounds

Compound		C found	C (calc)	H found	H (calc)	Br found	Br (calc)	S found	S (calc)
7a	$C_8H_9BrS_2$ (249.2)	38.6	(38.6)	3.5	(3.6)	32.2	(32.1)	25.6	(25.7)
7b	$C_8H_7BrS_2$ (247.2)	38.9	(38.9)	2.9	(2.9)	32.5	(32.3)	26.1	(25.9)
8a	$C_{16}H_{18}S_5$ (370.6)	52.0	(51.9)	4.9	(4.9)	-		43.4	(43.3)
8b	$C_{16}H_{14}S_5$ (366.6)	52.4	(52.4)	3.9	(3.9)	-		43.9	(43.7)
9a	$C_{16}H_{16}Br_2S_5$ (528.4)	35.9	(36.4)	3.0	(3.1)	30.4	(30.2)	30.3	(30.3)
9b	$C_{16}H_{12}Br_2S_5$ (524.4)	36.8	(36.7)	2.6	(2.3)	30.6	(30.5)	30.5	(30.5)
2a	$C_{16}H_{16}S_6$ (400.7)	48.0	(48.0)	4.0	(4.0)	-		48.0	(48.0)
2b	$C_{16}H_{12}S_6$ (396.7)	48.9	(48.5)	3.1	(3.1)	-		48.5	(48.5)

by refluxing the mixture of 18 h. Yield 33.9 g (50.4%), $bp_{2.5}$ 100–102°C (lit.:[19] $bp_{0.18}$ 82.5–85°C), n_D^{20} 1.6720 (lit.:[19] n_D^{25} 1.6713).

1-Bromo-3,4-bis(alkylthio)benzenes **7**: To 120 mmol 1,2-bis(alkylthio)benzene (**6**) in 400 ml dichloromethane the solution of 6.21 ml (19.4 g, 121.2 mmol) bromine in 100 ml dichloromethane is dropped with stirring within 3 h, the mixture then kept at room temperature for 20 h. Excess of bromine is removed by sodium sulfite, the product purified by distillation. **7a** (R = CH_3): Yield 29.5 g (98.6%), bp_2 113–115°C, n_D^{20} 1.6758. **7b** (R = 1/2 CH_2CH_2): Yield 23.3 g, 78.5%), bp_2 122°C, n_D^{20} 1.7009.

Bis[3,4-bis(alkylthio)phenyl]sulfides **8**: To the stirred solution of 120 mmol 1-bromo-3,4-bis(alkylthio)benzene (**7**) in 600 ml tetrahydrofuran (THF) 75 ml lithium *n*-butyl (1.6 M in *n*-hexane, 120 mmol) are dropped. After 15 min 18.8 g (60 mmol) bis(benzenesulfinyl)sulfide is added in small portions with vigorous stirring, the mixture kept at −78°C for a further 2 h, then allowed to warm to room temperature. The solvents are removed, the residue is solved in 300 ml dichloromethane, the solution washed with 3% aqueous potassium hydroxide and dried over magnesium sulfate. The mode of isolation depends on the alkylthio substituents. **8a** (R = CH_3): The residue of the dichloromethane solution is crystallized from ethanol. Yield 14.1 g (63.2%), mp. 99.5°C. **8b** (R = 1/2 CH_2CH_2): The residue, obtained as described, is purified by flash chromatography (cyclohexane/dichloromethane 4:1, R_F 0.17), yield 12.7 g (57.9%), highly viscous, honey-like product.

Bis[2-bromo-4,5-bis(alkylthio)phenyl]sulfides **9**: The solution of 2.6 ml (8.07 g, 50.5 mmol) bromine in 100 ml dichloromethane is added to the stirred solution of 25 mmol bis[3,4-bis(alkylthio)phenyl]sulfide (**8**). After 20 h the organic phase is washed in succession with aqueous sodium sulfite and hydrogencarbonate solutions, dried and evaporated. The residue is crystallized from trichloromethane/ethanol 2:1. **9a** (R = CH_3): Yield 11.9 g (89.9%), mp. 115°C. **9b** (R = 1/2 CH_2CH_2): Yield 8.5 g (64.3%), mp. 179°C.

2,3,7,8-Tetrakis(alkylthio)thianthrenes **2**: At −78°C 5.1 ml lithium *n*-butyl (1.6 M in *n*-hexane, 8.16 mmol) are dropped to the stirred solution of 4.0 mmol bis[2-bromo-4,5-bis(alkylthio)phenyl]sulfide (**9**) in 160 ml THF. After 30 min 1.26 g (4.0 mmol) bis(benzenesulfinyl)sulfide is added in small portions during 45 min. The mixture is stirred for further 2 h at −78°C, then allowed to warm to room temperature. THF is evaporated, the residue extracted with toluene and the toluene solution filtered over a small amount of basic aluminium oxide. The residue of the filtrate is extracted several times by boiling ethanol and then crystallized from ethanol/trichloromethane 1:2. **2a** (R = CH_3): Yield 401 mg (25.0%), mp. 183.5°C. **2b** (R = 1/2 CH_2CH_2): Yield 337 mg (21.2%), mp. 262.5°C.

Crystal structure determination. A Syntex $P2_1$ four-circle-diffractometer (Mo-Kα radiation with λ = 70.926 pm, $\omega/2\Theta$ scan mode with $4.5° \leq \Theta \leq 55°$, Lorentz and polarization corrections) and the programs SHELX-76,[20] SHELXS-86[21] are used for the X-ray analyses. The structures are determined by direct methods. Subsequent Fourier syntheses and full-matrix least-squares calculations allow all non-hydrogen atoms to be determined with anisotropic temperature factors. The positions of the hydrogen atoms are calculated with fixed distances of 96 pm and isotropic temperature factors.

All crystallographic data have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen and are available on quoting the depository number CSD-57686, the names of the authors, and the journal citation.

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