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Organometalloidal Compounds with *o*-Phenylene Substituents. Part 29.[1] Reaction of Sulfur Dichloride with 2-Methoxyphenol: Isolation and Characterization of 2,8-Dihydroxy-3,7-dimethoxy- and 1,6-Dichloro-2,7-dihydroxy-3,8-dimethoxy-thianthrene

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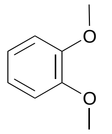
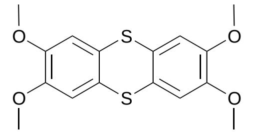
From 2-methoxyphenol (**4**) and sulfur dichloride a wealth of compounds are formed, but the reaction conditions can be varied in such a way that either 2,8-dihydroxy-3,7-dimethoxythianthrene (**9**) or 1,6-dichloro-2,7-dihydroxy-3,8-dimethoxythianthrene (**10**) is formed predominantly; both compounds are characterized by X-ray crystallographic analysis.

Aromatic systems possessing two activating substituents in the *ortho*-positions react with sulfur dichloride to form thianthrenes. Thus, from 1,2-dimethoxybenzene (**1**), 2,3,7,8-tetramethoxythianthrene (**2**) is obtained.[2] From systems like **3** with two different substituents, two isomers, one, **7**, with a *cisoid*, the other, **8**, with a *transoid* arrangement of the substituents, are to be expected. According to Scheme 1 the predominant formation of **7** is favoured by a quick addition of sulfur dichloride to **3**, provided the activation by R in comparison with R* is stronger. In contrast, isomer **8** is favoured by a slow addition of sulfur dichloride.



1



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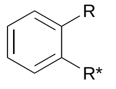

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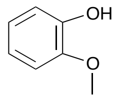

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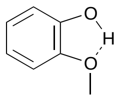
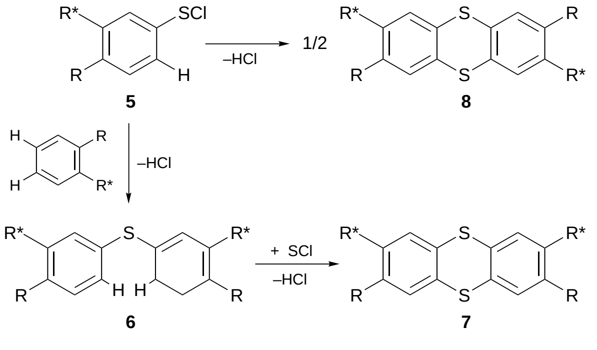


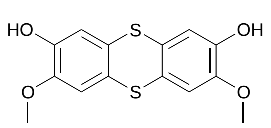
4a

In this paper the reaction of sulfur dichloride with 2-methoxyphenol (**4**) is studied. Although the hydroxy and methoxy substituents show similar electronic effects in electrophilic substitution reactions,[4,5] the behaviour of **4** according to Scheme 1 seemed possible, since, owing to the *ortho*-positions of the two competing substituents, an intramolecular hydrogen bond, as in **4a**, can be formed, which would lead to attack at the position *para* to the hydroxy group being favoured.

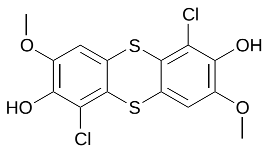
Indeed, when sulfur dichloride was slowly added to 2-methoxyphenol (**4**), in glacial acetic acid, 2,8-dihydroxy-3,7-dimethoxythianthrene (**9**) was the predominant product. However, when an excess of sulfur dichloride was added rapidly, mainly 1,6-dichloro-2,7-dihydroxy-3,8-dimethoxythianthrene (**10**) was formed, *i.e.* the expected *transoid*-substituted thianthrene (corresponding to **8**), but it is chlorinated in the addition, probably through the equilibrium[16] $2SCl_2 \rightleftarrows S_2Cl_2 + Cl_2$.



Scheme 1



9



10

Both compounds were characterized by crystal structure determination. Suitable single crystals in form of the solvate **9**·acetone and **10**·2THF were measured at 170 K on a CAD4 four-circle diffractometer using Cu-Kα radiation ($\lambda = 154$ and 178 pm) and were corrected for Lorentz and polarization factors. The structures were solved by direct methods.[17] Subsequent Fourier syntheses and LSQ calculations[18] allowed the positions of all non-hydrogen atoms and, in addition, of the hydrogen atoms at the hydroxy groups to be determined; these atom positions were refined by anisotropic temperature factors. The positions of the other hydrogen atoms were calculated with fixed distances of 96 pm and isotropic temperature factors. The results are summarized in Tables 1, 4 and 5.

As is typical for thianthrene derivatives the molecules of **9** and **10** are folded at their SS axes, the angles of fold (defined

Table 1 Crystal structure parameters for **9**·acetone and **10**·2THF

	9·acetone	**10**·2THF
Empirical formula	$C_{14}H_{12}O_4S_2 \cdot C_3H_6O$	$C_{14}H_{10}Cl_2O_4S_2 \cdot 2C_4H_8O$
Crystal system	monoclinic P	monoclinic P
Space group	$P2_1/m$	$P2_1/n$
a/pm	608.4(1)	1780.1(5)
b/pm	1384.3(2)	808.1(2)
c/pm	1050.4(2)	1828.8(6)
β/°	103.38(2)	117.66(2)
Z	2	4
M_r	366.45	521.48
$V/10^6$ pm^3	860.6(2)	2330(1)
ρ/g cm^{-3}	1.414	1.486
μ/cm^{-1}	29.7	45.2
Scan range/°	$4.5 < 2\theta < 153$	$4.5 < 2\theta < 153$
Independent reflections	1738	4298
Reflections with $\lvert F_0 \rvert > 4\sigma(\lvert F \rvert)$	1721	4266
Refined parameters	130	300
R_1, R_2	0.041, 0.047	0.057, 0.061

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*To receive any correspondence.

Table 4 Relevant bond lengths (pm) in **9**·acetone and **10**·2THF (mean values)

	9·acetone	**10**·2THF
C—Cl	—	173.5(3)
C—S	177.0(2)	177.0(3)
C_{ar}—O	135.9(2)	135.7(4)
C_{alk}—O	142.3(3)	143.0(4)
(S)C—C(S)	138.9(3)	139.7(4)
(S)C—C	139.8(3)	139.4(5)
(O)C—C	138.3(3)	138.0(5)
(O)C—C(O)	141.1(3)	141.2(5)
O—H	86(3)	80(4)
$O\cdots H_{intra}$	220	230
$O\cdots H_{inter}$	196	189

Table 5 Bond angles (°) in **9**·acetone and **10**·2THF (mean values)

	9·acetone	**10**·2THF
C—S—C	100.5(1)	100.8(1)
C—O—C	117.9(1)	117.1(2)
C—O—H	108(2)	114(2)
Cl—C—C(S)	—	120.3(2)
Cl—C—C(O)	—	117.7(2)
S—C—C_{endo}	120.8(1)	120.8(2)
S—C—$C(H)_{exo}$	119.4(1)	118.3(2)
S—C—$C(Cl)_{exo}$	—	121.3(2)
$O(CH_3)$—C—C_{endo}	125.9(1)	125.9(3)
$O(CH_3)$—C—C_{exo}	114.3(1)	113.8(3)
O(H)—C—C_{endo}	121.3(1)	121.4(3)
O(H)—C—C_{exo}	119.0(1)	119.6(2)
C(H)—C(S)—C(S)	119.9(1)	120.5(3)
C(Cl)—C(S)—C(S)	—	118.5(3)
C(S)—C(H)—C(O)	120.3(1)	120.1(3)
C(S)—C(Cl)—C(O)	—	122.0(3)
C(H)—C(O)—C(O)	119.8(1)	120.4(3)
C(Cl)—C(O)—C(O)	—	118.6(3)
$O—H\cdots O_{intra}$	115	110
$O—H\cdots O_{inter}$	150	157

as angles between the normals to the best planes through the aryl rings) being 134.8 and 132.1°, respectively (Figs. 1 and 2).

The methoxy and hydroxy substituents are coplanar with the aryl rings to which they belong. Whereas the methoxy group is turned to the outside position, the hydroxy group lies inside forming an intramolecular hydrogen bridge to the oxygen atom of the methoxy group. Owing to steric repulsion the angles OCC (*endo*) are larger than the corresponding *exo* ones, the effect being more pronounced for the methoxy groups. In comparison to **9**, the introduction of the chloro substituents into **10** causes differentiation of the corresponding angles, especially in the C_6 rings (Table 5).

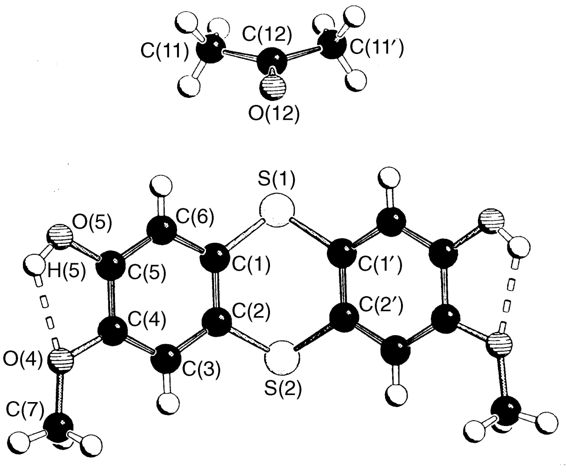

Fig. 1 Molecular structure of **9**·acetone

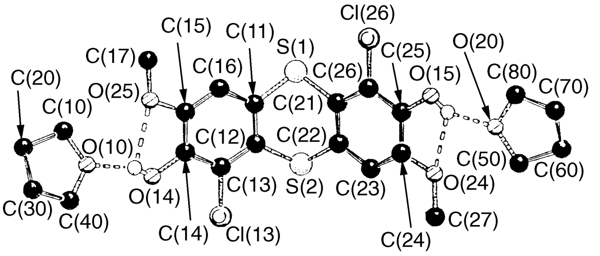

Fig. 2 Molecular structure of **10**·2THF

All distances lie in the normal ranges (Table 4) and no different influence of the methoxy and hydroxy substituents can be observed, though they differ in their kinetic effects as can be seen from the syntheses of **9** and **10**.

In the crystals the hydroxy groups also form intermolecular hydrogen bonds to the solvate molecules. In **9**·acetone an infinite chain of alternating thianthrene and acetone molecules is formed (Fig. 3) since the oxygen atom of each acetone molecule is involved in two hydrogen bridges. In **10**·2THF the crystal is built up by isolated THF···**10**···THF units.

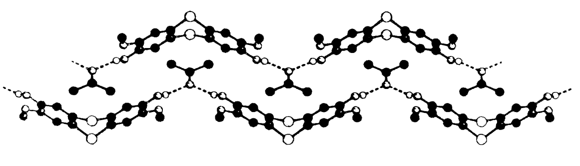

Fig. 3 Infinite chains of alternating thianthrene and acetone molecules in the crystal of **9**·acetone

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Full text in German

Techniques used: IR, ^1H and ^{13}C NMR, X-ray analysis

References: 20

Tables 2 and 3: Atomic coordinates and equivalent isotropic thermal parameters for **9**·acetone and **10**·2THF

Fig. 4: Arrangement of the THF···**10**···THF units in the crystal of **10**·2THF

Schemes 2 and 3: Probable reaction paths leading to **9** and **10**

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