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The title compounds **5** were obtained from the reaction of 3,3',4,4'-tetramethoxybiphenyl (**6**) or its 2,2'-dilithio derivative **8** with various chalcogen electrophiles (sulfur dichloride, selenium tetrachloride, selenium oxychloride and tellurium tetrachloride).

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A variety of heterocyclic compounds containing sulfur [1] and [2]/or [3] selenium or tellurium [4] have recently found extensive use as donor components for the preparation of charge transfer complexes and ion radical salts of high electrical conductivity.

Much interest has been focused on the tetraheterofulvalene derivatives **1** and Bechgaard [5] has recently prepared superconducting crystals of the cation radical salt bis-(tetramethylselenafulvalenium) perchlorate, (TMTSF)₂ perchlorate (TMTSF = **1**, X = Se, R = CH₃).

Several other systems have also attracted attention and it has been of particular interest to study the role of increasing chalcogen substitution (sulfur, selenium, tellurium) in the donor, for a specific donor/acceptor complex.

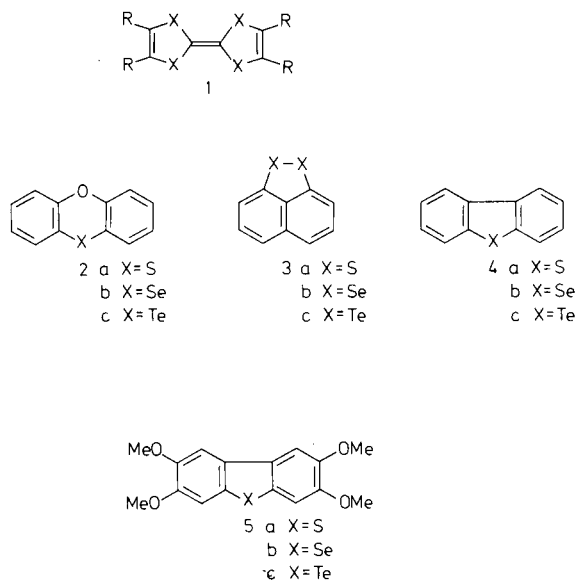
A study of the phenoxachalcogenines **2** as donors towards 7,7,8,8-tetracyanoquinodimethane (TCNQ) did not reveal any significant improvement in the conductivity in going from sulfur (**2a**) to tellurium (**2c**) [6]. However, some other reports do suggest that considerable enhancements in electronic properties are possible:

The dichalcogenide bridged 1,8-naphthalenes **3** showed an increasing conductivity of the TCNQ charge transfer complexes in going from sulfur (**3a**, $\sigma = 10^{-11}$ ohm⁻¹cm⁻¹) through selenium (**3b**, $\sigma = 5 \cdot 10^{-8}$ ohm⁻¹cm⁻¹) to tellurium (**3c**, $\sigma = 2 \cdot 10^{-2}$ ohm⁻¹cm⁻¹) [7]. The compounds **4** showed a seven orders of magnitude improvement in conductivity in going from dibenzoselenophene (**4b**) to dibenzotellurophene (**4c**) [8].

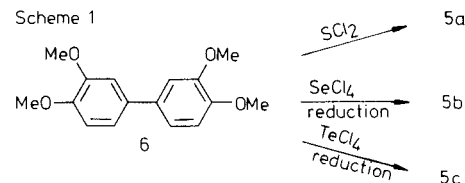
The conductivity of a charge transfer salt is related to the ionization potential of the donor. A lowering of the ionization potential is usually accompanied by an increase in conductivity. This is true for the series **3** and **4** above, but exceptions to this rule do exist [9]. We felt that it might be of interest to lower the oxidation potential in the series **4** above, by methoxy substitution, to see how this would influence the conductivities of the charge transfer salts.

In the following we report various synthetic approaches towards the homologous series **5**, containing four methoxy groups in the positions 2, 3, 7 and 8. 2,3,7,8-Tetramethoxydibenzothiophene (**5a**) is the only known compound in the

series, but it is only available in poor yield *via* a lengthy procedure [10]. We initially wanted to synthesize all three compounds from the same starting material, 3,3',4,4'-tetramethoxybiphenyl (**6**), using various chalcogen electrophiles as shown in Scheme 1.

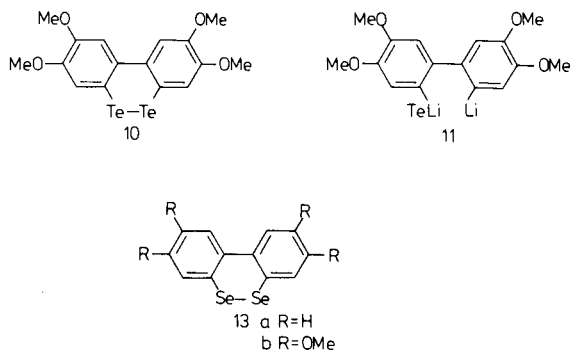
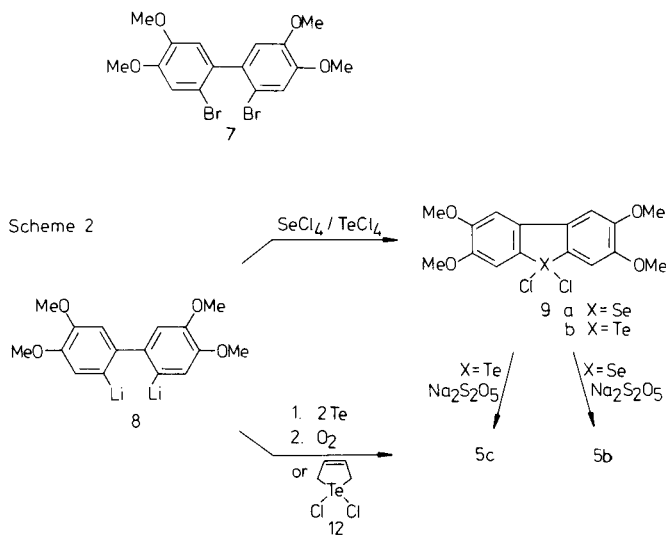


Scheme 1



3,3',4,4'-Tetramethoxybiphenyl is available *via* an Ullman coupling of 4-iodoveratrol and its reaction with sulfur dichloride afforded compound **5a** in 90% yield, simply by mixing of the reactants in chloroform. However, neither tellurium tetrachloride nor selenium tetrachloride or selenium oxychloride reacted in the desired manner to produce compounds **5c** and **5b**, respectively. Instead, chlor-

ination of the biphenyl seemed to be the preferred reaction. We therefore decided to use 2,2'-dibromo-4,4',5,5'-tetramethoxybiphenyl (**7**) as our substrate. Compound **7** is readily available *via* bromination of 3,3',4,4'-tetramethoxybiphenyl in acetic acid [11]. Our strategy was to allow the 2,2'-dilithiated biphenyl **8** to react with selenium tetrachloride and tellurium tetrachloride, respectively, to give the 5,5-dichlorides **9** of compounds **5b** and **5c** (Scheme 2). Compound **7** was dilithiated in tetrahydrofuran using two equivalents of *t*-butyllithium at 0°. After addition of selenium tetrachloride and tellurium tetrachloride, respectively, the reaction mixtures were reduced with aqueous sodium disulphite without isolation of the 5,5-dichlorides **9**. In this way 2,3,7,8-tetramethoxydibenzoselenophene (**5b**) and 2,3,7,8-tetramethoxydibenzotellurophene (**5c**) were isolated in 8 and 3% yield, respectively. The replacement of selenium tetrachloride by selenium oxychloride did not improve the yield of compound **5b**. However, the yield of 2,3,7,8-tetramethoxydibenzotellurophene (**5c**) could be improved to 16% using the series of reactions described in the lower part of Scheme 2.



To the dilithio compound **8** in tetrahydrofuran was added two equivalents of finely ground elemental tellurium.

After 5 hours of stirring, oxygen was passed through the reaction mixture for 1 hour, followed by aqueous work-up. It is well-known that elemental tellurium readily inserts into carbon-lithium bonds [12]. The formation of compound **5c** can be rationalized assuming a double tellurium insertion followed by oxidation to an unstable 1,2-ditellurin **10**, which spontaneously is extruding tellurium to give the aromatic compound **5c**. Alternatively, only monoinsertion of tellurium occurs, followed by oxidative ring-closure of compound **11**. The dilithio compound **8** was allowed to react also with 1,1-dichloro-2,5-dihydro-2,5-dithiophene (**12**), as shown in Scheme 2. Compound **12** is known to readily lose butadiene on treatment with Grignard reagents and it is thus functioning as a tellurium dichloride equivalent [13]. However, the yield of compound **5c** was still very modest (13%). The new methods of dibenzotellurophene synthesis were also applied for the construction of dibenzotellurophene (**4c**) itself. 2,2'-Dilithiobiphenyl afforded dibenzotellurophene in 25% yield on treatment with elemental tellurium and oxygen and the yield could be raised to a respectable 78% when 1,1-dichloro-2,5-dihydro-2,5-dithiophene was used.

The replacement of elemental tellurium by elemental selenium in the reaction sequence described in the lower part of Scheme 2 did not yield a dibenzoselenophene. Instead, the new compound 2,3,8,9-tetramethoxydibenzo-*[c,e]*[1,2]diselenin (**13b**) was isolated in low yield (4%). 2,2'-Dilithiobiphenyl similarly afforded the new compound **13a** in 32% yield. These products are apparently formed by a double Se insertion followed by oxidation to give a diselenide linkage.

As expected, all three compounds **5** are easily oxidized to give deep blue-coloured radical cations. This can be seen by dissolving a small crystal in concentrated sulfuric acid. Apparently, oxidation even occurs to a small extent on a silica column since the compounds are moving as faint blue bands during elution. The three compounds **5** all form crystalline 1:1 complexes with TCNQ and their electrical properties are presently being investigated.

EXPERIMENTAL

Melting points were uncorrected. The nmr spectra were recorded using a Bruker WP 200 instrument. Unless otherwise stated, deuteriochloroform was used as solvent containing tetramethylsilane as the internal standard. Elemental analyses were performed by Centrala Analyslaboratoriet, Uppsala, Sweden.

3,3',4,4'-Tetramethoxybiphenyl [14], 2,2'-dibromo-4,4',5,5'-tetramethoxybiphenyl [11], 2,2'-dibromobiphenyl [15] and 1,1-dichloro-2,5-dihydro-2,5-dithiophene [13] were synthesized according to literature methods.

2,3,7,8-Tetramethoxydibenzothiophene (**5a**).

Sulfur dichloride (0.38 g, 3.69 mmoles) in 10 ml of chloroform was added dropwise to a stirred solution of 1.0 g (3.65 mmoles) of **6** in 10 ml of chloroform at 0°. The reaction mixture was then stirred overnight at ambient temperature. Evaporation and chromatography (methylene

chloride) afforded 1.0 g (90%) of **5a**, mp 193-194° (ethanol) lit 188-190° [10]; nmr (dimethylsulfoxide-D6): δ 3.84 (s, OCH₃, 6 H), 3.92 (s, OCH₃, 6 H), 7.52 (s, aromatic, 2 H), 7.85 (s, aromatic 2 H).

2,3,7,8-Tetramethoxydibenzoselenophene (**5b**).

Two and one half ml of 1.7 M *t*-butyllithium (4.25 mmoles) in pentane was added dropwise under nitrogen to a stirred solution of 0.81 g (1.9 mmoles) of **7** in 50 ml of dry tetrahydrofuran at 0°. After 30 minutes, 0.41 g (1.9 mmoles) of selenium tetrachloride in 5 ml of dry tetrahydrofuran was added and stirring continued for 2 hours at ambient temperature. After evaporation the product was shaken with methylene chloride and a 10% aqueous sodium sulphite solution to reduce all selenium(IV) compounds. Chromatography (methylene chloride) of the organic material obtained after separation, drying and evaporation afforded an inseparable mixture of compounds **5b** and **6**. However, only compound **5b** formed a charge transfer complex with TCNQ. The mixture was therefore dissolved in a small amount of acetonitrile and 0.055 g of TCNQ was added. The precipitated charge transfer complex was chromatographed (methylene chloride) to yield 0.053 g (8%) of **5b** as white crystals, mp 180-181° (ethanol); nmr: δ 3.97 (s, OCH₃, 6 H), 4.04 (s, OCH₃, 6 H), 7.31 (s, aromatic, 2 H), 7.41 (s, aromatic, 2 H).

Anal. Calcd. for C₁₆H₁₆O₄Se: C, 54.71; H, 4.59. Found: C, 54.59; H, 4.62.

2,3,7,8-Tetramethoxydibenzotellurophene (**5c**).

A solution of **8** in 50 ml of tetrahydrofuran was prepared as described above from 3.0 ml of 1.7 M *t*-butyllithium (5.1 mmoles) and 1.0 g (2.3 mmoles) of **7**. After 30 minutes, 0.59 g, (4.6 mmoles) finely ground elemental tellurium was added and stirring continued for 5 hours at ambient temperature. Oxygen was then passed through the solution for 1 hour. After evaporation, extraction with methylene chloride/water and chromatography (methylene chloride), compounds **5c** and **6** were obtained as an inseparable mixture. Recrystallization from ethyl ether/methylene chloride afforded 0.15 g (16%) of pure **5c**, mp 190-191° (ethanol). Alternatively, separation could be effected by preparation of the TCNQ complex as described above; nmr: δ 3.95 (s, OCH₃, 6 H), 4.03 (s, OCH₃, 6H), 7.29 (s, aromatic, 2 H), 7.38 (s, aromatic, 2 H).

Anal. Calcd. for C₁₆H₁₆O₄Te: C, 48.06; H, 4.03. Found: C, 47.68; H, 3.96.

When compound **8** (2.3 mmoles) was allowed to react with a stoichiometric amount of **12** for 2 hours at ambient temperature in tetrahydrofuran, 0.12 g (13%) of compound **5c** was obtained after the usual work-up procedure (no oxygen bubbling). When tellurium tetrachloride similarly was used as the electrophile (with sodium disulphite reduction), only a 3% yield of **5c** was isolated.

Dibenzotellurophene (**4c**).

By analogy with the preparation of **5c**, 2,2'-dilithiobiphenyl was prepared from 4.0 ml of 1.7 M *t*-butyllithium (6.8 mmoles) and 1.0 g (3.2 mmoles) of 2,2'-dibromobiphenyl. After addition of 0.82 g (6.4 mmoles) of elemental tellurium, stirring, oxygen bubbling and work-up as described above, 0.22 g (25%) of **4c**, mp 92-93° (lit 93°) [16], was isolated after chromatography.

In another attempt 0.41 g (1.6 mmoles) of **12** in dry tetrahydrofuran was added to a solution of 2,2'-dilithiobiphenyl (1.6 mmoles) at 0°. After 2 hours at ambient temperature, 0.35 g (78%) of **4c** was obtained.

In another attempt 0.41 g (1.6 mmoles) of **12** in dry tetrahydrofuran was added to a solution of 2,2'-dilithiobiphenyl (1.6 mmoles) at 0°. After 2 hours at ambient temperature, 0.35 g (78%) of **4c** was obtained.

Dibenzo[*c,e*]1,2]diselenin (**13a**).

2,2'-Dilithiobiphenyl was prepared as described above from 0.50 g (1.6 mmoles) of 2,2'-dibromobiphenyl and 2.0 ml of 1.7 M *t*-butyllithium (3.4 mmoles). Finely ground elemental selenium (0.26 g, 3.3 mmoles) was then added and oxygen passed through the solution after 30 minutes of stirring. Evaporation and extraction with methylene chloride afforded 0.12 g

(32%) of compound **13a** after chromatography (light petroleum bp 40-60°/methylene chloride = 9/1) mp 114-115° (ligroin); nmr: δ 7.23 (m, aromatic, 2 H), 7.35 (m, aromatic, 2 H), 7.63 (d, aromatic, 2 H), 7.73 (d, aromatic, 2 H).

Anal. Calcd. for C₁₂H₈Se₂: C, 46.48; H, 2.60. Found: C, 46.67; H, 2.67.

2,3,8,9-Tetramethoxydibenzo[*c,e*]1,2]diselenin (**13b**).

Compound **8** was prepared as described above from 2.0 ml of 1.7 M *t*-butyllithium (3.4 mmoles) and 0.70 g (1.6 mmoles) of **7**. To this solution was added 0.26 g (3.3 mmoles) of selenium and continued according to the procedure for **13a**. Chromatography (methylene chloride) afforded 0.026 g (4%) of **13b**, mp 208°; nmr: δ 3.93 (s, OCH₃, 6 H), 3.95 (s, OCH₃, 6 H), 7.08 (s, aromatic, 2 H), 7.21 (s, aromatic, 2 H).

Anal. Calcd. for C₁₆H₁₆O₄Se₂: C, 44.67; H, 3.75. Found: C, 45.06; H, 3.84.

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