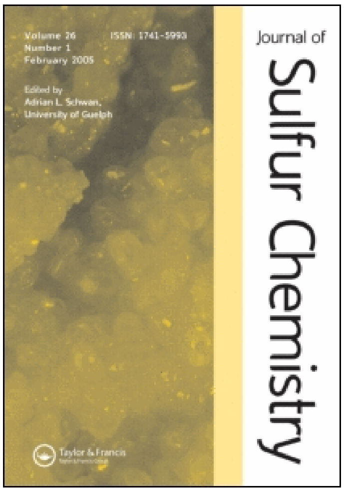

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Synthesis, Reactions, and Selected Physico-Chemical Properties of 1,3-and 1,2-Tetrachalcogenafulvalenes

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SYNTHESIS, REACTIONS, AND SELECTED PHYSICO-CHEMICAL PROPERTIES OF 1,3- AND 1,2-TETRACHALCOGENAFULVALENES

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(Received 11 July 1986)

This review describes the synthesis of 1,3-tetrachalcogenafulvalenes and 1,2-tretrathiafulvalenes, the chemical transformation of substituents, reactions of the ring system, and the synthesis of polymers with 1,3-tetrathiafulvalene units in the backbone and in the side chain. 1,2- And 1,3-tetrachalcogenafulvalenes synthesized until now and selected properties (melting point, u.v.-vis. absorption data and oxidation potential) are recorded in appropriate tables. The literature until the end of 1985 is taken into account.

Preparations of important starting compounds for the synthesis of tetrachalcogenafulvalenes (like 1,2- and 1,3-dithiole, 1,3-thiaselenole, and 1,3-diselenole derivatives) have been considered in this review. For selected charge-transfer complexes of tetrachalcogenafulvalenes the relation between molecule structure and solid-state structure, respectively, and electric conductivity are discussed. Other physical properties of the solid state of the complexes were not considered. Possibilities for the application of these charge-transfer complexes are also mentioned.

Key words: Tetrachalcogenafulvalenes, TTF, polymeric TTF, synthesis, electric conductivity, charge-transfer complexes.

CONTENTS

INTRODUCTION

Tetrachalcogenafulvalenes are electron donors which easily form charge-transfer complexes with electron acceptors like tetracyanoquinodimethane (TCNQ), bromine, or iodine, respectively. These complexes are radical salts. Among them those are of special interest which possess a segregated stack structure. They are so-called organic metals, a topic which is reflected in many reviews and monographs.[1–16] Systematic investigation of the relation between the structure and the properties of tetrachalcogenafulvalene complexes, as well as the discovery of radical salts with superconductivity and an increase of their critical temperature in the last years, (from 1 K[17] to 5 K[9,18]) has strongly stimulated efforts to find efficient preparationsfor tetrachalcogenafulvalenes and also for the corresponding starting materials. Since the publication of the first review concerning the preparation and the properties of these donors by Narita and Pittman in 1976,[19] many new tetrathiafulvalenes and tetraselenafulvalenes have been synthesized, new methods for synthesis and new possibilities to modify these compounds have been described. New types of donors like 1,2-tetrathiafulvalenes and 1,3-tetratellurafulvalenes have been found. In this review a survey of the development in this field in the last ten years is given, taking also some older publications into account.

After the completion of this manuscript two new reviews concerning especially the synthesis of tetrathiafulvalenes were published.[20]

1. SYNTHESIS OF TETRATHIAFULVALENES (TTF)

1.1. 1,3-Dithiole-2-thiones and -selones as Starting Materials for TTF

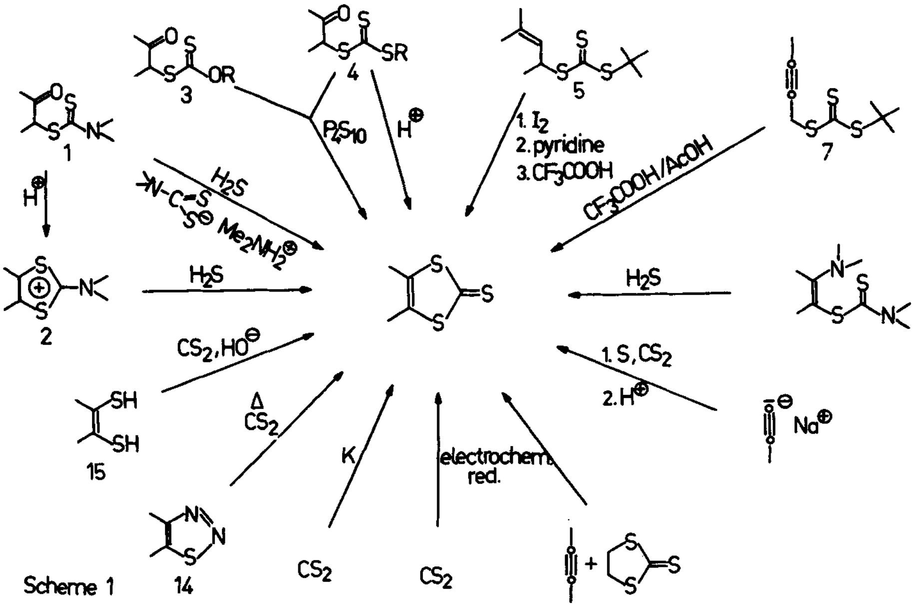
In the last years some methods for the synthesis of TTF have been developed. The most important methods start with 1,3-dithiole derivatives which are converted into TTF in different ways. Therefore the synthesis of 1,3-dithiole-2-thiones, the precursors of 1,3-dithiole derivatives, is important. Possibilities for their synthesis are summarized in Scheme 1.

With a large variety of substituents the cyclization of β-keto-*N*,*N*-dialkyldithiocarbamates **1** with concentrated sulfuric acid or 70 % perchloric acid and subsequent treatment of the so formed 2-amino-1,3-dithiolium salts **2** with hydrogen sulfide in pyridine or methanol gives high yields.[21–23]

The corresponding β-keto-*N*,*N*-dialkyldithiocarbamate **1** is cyclized directly to 4,5-tetramethylene-1,3-dithiole-2-thione with hydrogen sulfide in methanol in the presence of dimethylammonium-*N*,*N*-dimethyldithiocarbamate as catalyst in satisfactory yield (66 %), too.[24]

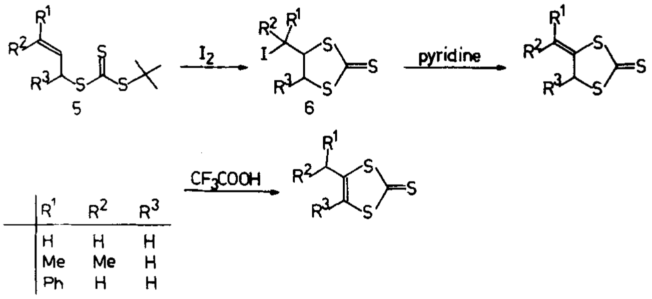
The cyclization of β-keto-*O*-alkyldithiocarbonates **3** or β-keto-*S*-alkyltrithiocarbonates **4** succeeds with phosphorus pentasulfide in boiling decaline.[25–28] In the case of β-keto-*S*-*t*-butyltrithiocarbonates **4** the cyclization takes place with higher yields with a mixture of trifluoroacetic acid and acetic acid.[29]

The readily available allyl halides can be easily converted with high yields into



Scheme 1

differently substituted 1,3-dithiole-2-thiones with sodium *t*-butyltrithiocarbonate in a multistep reaction. The corresponding allyl *t*-butyl trithiocarbonate **5** is cyclized with iodine with concomitant loss of isobutylene and hydrogen iodide. In the next steps the

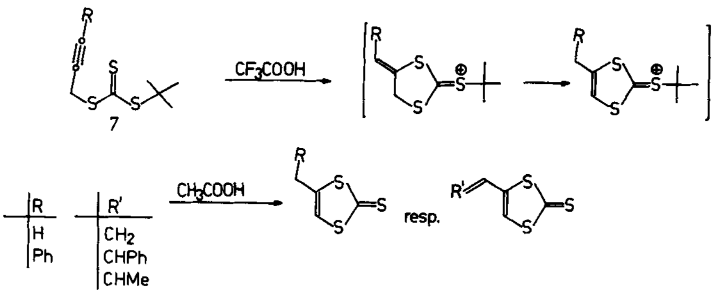


R^1	R^2	R^3
H	H	H
Me	Me	H
Ph	H	H

elimination of hydrogen iodide with pyridine from the 1,3-ditholane-2-thione **6** and the isomerization of the double bond with trifluoroacetic acid takes place.[30]

In a similar manner, 1,3-dithiole-2-thiones are formed in high yields in a one-step reaction by ring closure of propargyl *t*-butyl trithiocarbonates **7** with trifluoroacetic acid in glacial acetic acid. When acetylenic alcohols ($R = R'\overset{|}{C}HOH$) are employed in the reaction sequence dehydration occurs, resulting in the formation of vinyl-1,3-dithiole-2-thiones.[31]

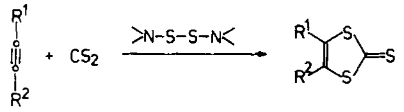
Enamines are substituted in the 2-position by tetramethylthiuram disulfide in the presence of triethylamine and the products cyclized by passing hydrogen sulfide through the reaction mixture. Enamines of cyclic or aryl substituted ketones give 1,3-dithiole-2-thiones with good yields (35–90%). Enamines of aliphatic aldehydes do not react. With



R	R'
H	CH$_2$
Ph	CHPh
	CHMe

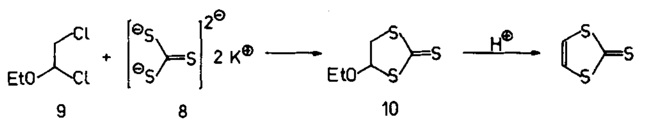
ketimines of acyclic dialkyl ketones the reaction occurs. Indeed, the yields of 1,3-dithiole-2-thiones are moderate (10–35%).[24]

The reaction between acetylenes and carbon disulfide in the presence of bisamino disulfides in a Parr bomb reactor at 140 °C provides the corresponding 1,3-dithiole-2-thiones.[32] The unsubstituted 1,3-dithiole-2-thione is formed in 25% yield in a one-step synthesis upon treatment of sodium acetylide with sulfur and carbon disulfide.[33]



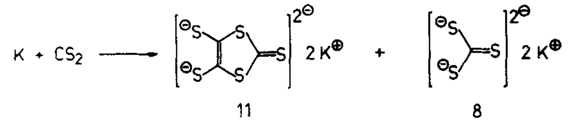
R^1	Ph	t-Bu	Ph	H	COOMe
R^2	H	H	COOEt	COOMe	COOMe

Higher yields of the unsubstituted 1,3-dithiole-2-thione are obtained in the reaction of dimethyl acetylenedicarboxylate with 1,3-dithiolane-2-thione, followed by hydrolysis and decarboxylation of the 4,5-bis(carbomethoxy)-1,3-dithole-2-thione formed.[34] The reaction of acetylenes with 1,3-dithiolane-2-thione proceeds only in the case of acetylenes with electron-withdrawing substituents (–COOR, –CF$_3$, –CN, –CHO).[35,36] A good yield of unsubstituted 1, 3-dithiole-2-thione is obtained in a two-step synthesis, starting from potassium trithiocarbonate **8** and 1,2-dichloroethyl ethyl ether **9**. The 4-ethoxy-1,3-dithiolane-2-thione **10** formed is converted into the 1,3-dithiole-2-thione by elimination of ethanol with *p*-toluenesulfonic acid.[37]

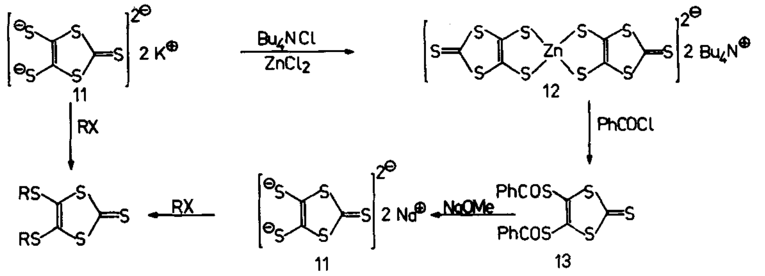


The electrochemical reduction of carbon disulfide on a mercury or platinum electrode in *N*,*N*-dimethylformamide provides the 4,5-dimercapto-1,3-dithiole-2-thione dianion **11**, which with alkylating agents can form 4,5-bis(alkylthio)-1,3-dithiole-2-thiones.[38–40] On a preparative scale it is better to reduce carbon disulfide with chemical reducing agents. Reduction with potassium in *N*,*N*-dimethylformamide gives the highest yields.[41]

In the electrochemical as well as in the chemical reduction appreciable amounts of trithiocarbonate **8** are formed. The 4,5-dimercapto-1,3-dithiole-2-thione dianion **11** can



be separated from the trithiocarbonate **8** as the tetrabutylammonium zinc chelate **12**.[42,43] **12** is converted into 4,5-bis(benzoylthio)-1,3-dithiole-2-thione **13**, then to 4,5-dimercapto-1,3-dithiole-2-thione dianion **11** by cleavage with sodium methoxide and afterwards



by alkylation to 4,5-bis(alkylthio)-1,3-dithiole-2-thiones.[44] After the reduction the reaction mixture can be alkylated directly, too, so that a separation of **11** from **8** is not necessary.[41]

Thermolysis of 1,2,3-thiadiazole **14** under pressure at 220 °C in carbon disulfide allows the synthesis of trimethylene- and tetramethylene-1,3-dithiole-2-thione in moderate yields (41 resp. 43%) and of benzo-1,3-dithiole-2-thione in good yield (84%).[45,46]

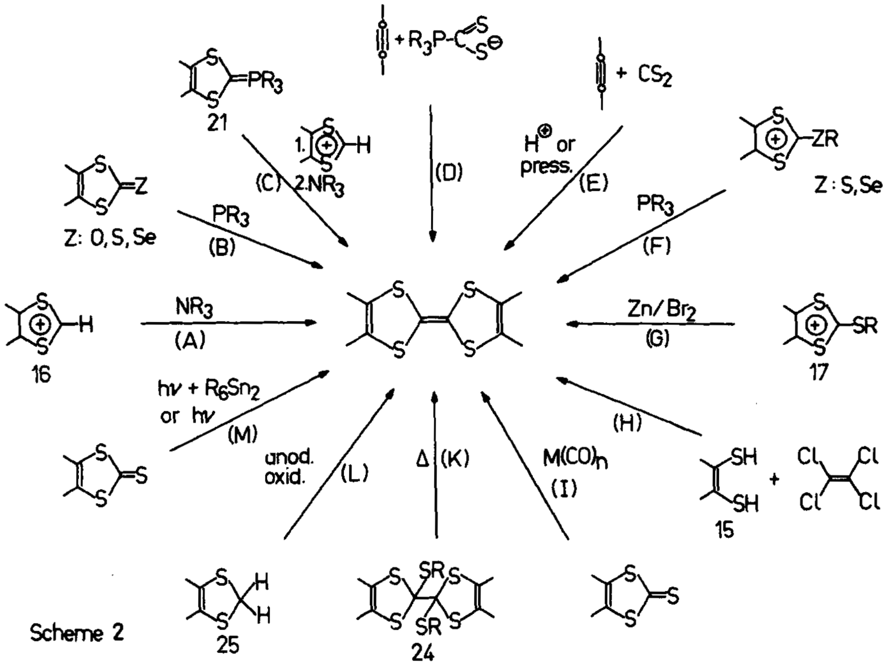
Benzo-annelated and heterocyclo substituted 1,3-dithiole-2-thiones are formed by treatment of the 1,2-dimercapto compounds **15** with carbon disulfide in alkaline solution or with thiocarbonyldiimidazole in glacial acetic acid/tetrahydrofuran.[47-50]

The synthesized 1,3-dithiole-2-thiones can be converted into TTF in different ways. The most important methods are summarized in Scheme 2.

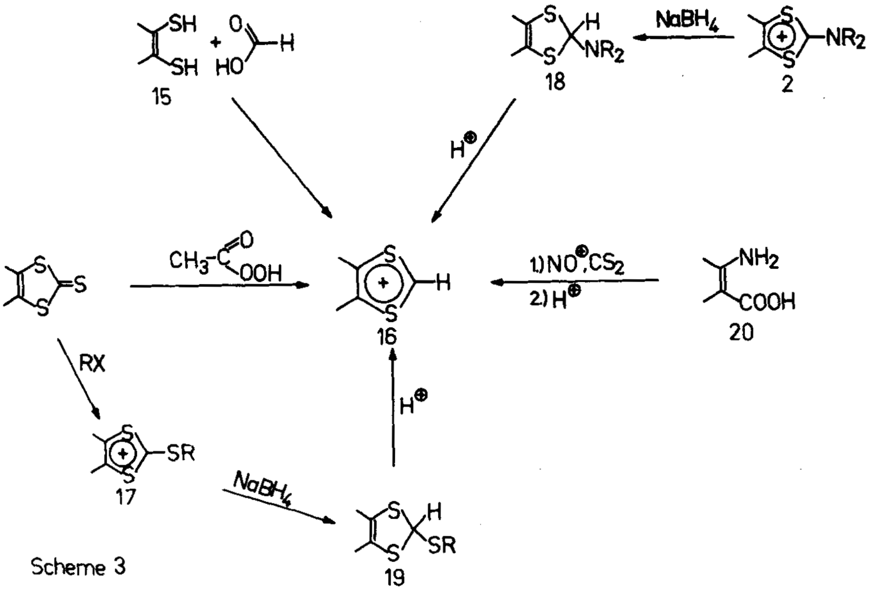
1.2. TTF by Deprotonation of 1,3-Dithiolium Salts (Method A)

Treatment of 1,3-dithiolium salts **16** with tertiary aliphatic amines (*N*-ethyldiisopropylamine, triethylamine) in acetonitrile provides TTF in large quantities. By using unsymmetrically substituted 1,3-dithiolium salts **16** a mixture of *cis*- and *trans*-isomers is formed. The isomers cannot be separated because of the negligible difference in their properties. This mixture of *cis*- and *trans*-isomers is also formed by all other methods of TTF synthesis, starting with differently substituted 1,3-dithiole derivatives. 1,3-Dithiolium salts are stable compounds because the 1,3-dithiolium cation is resonance stabilized. They can be prepared in different ways (Scheme 3).[51,52]

1,3-Dithiolium salts **16** with donor substituents or one acceptor substituent and the unsubstituted 1,3-dithiolium salt can be formed by oxidizing the corresponding 1,3-dithiole-2-thione with peracetic acid in acetone or with hydrogen peroxide in glacial acetic acid.[25,53] 1,3-Dithiole-2-thiones with acceptor substituents in the 4- and 5-position cannot be converted into 1,3-dithiolium salts **16** in this way.[53] TTF with electron-withdrawing substituents are formed in high yields by method B.



Scheme 2



Scheme 3

2-*N*,*N*-Dialkylamino- and 2-alkylthio-1,3-dithiolium salts **2** resp. **17** are converted into 1,3-dithiolium salts **16** by reduction with sodium borohydride, followed by treatment with acid.[22,54,55]

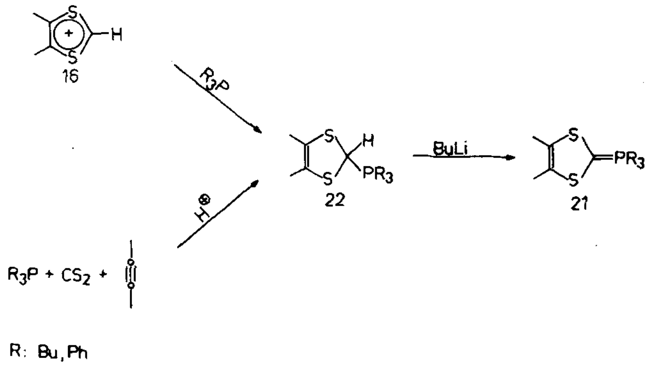
Benzo- or naphtho-annelated 1,3-dithiolium salts **16** are obtained by the reaction of the 1,2-dimercapto compounds **15** with formic acid[56–59] or by that of 2-aminocarboxylic acids **20** with isopentyl nitrite in 1,2-dichloroethane in the presence of carbon disulfide and treatment of the obtained 2-isopentyl-1,3-dithiole with acid.[60] Naphtho-annelated or heterocyclo substituted 1,3-dithiolium salts **16** are also formed in large quantities by alkylation of the corresponding 1,3-dithiole-2-thiones, reduction of the so prepared 2-alkylthio-1,3-dithiolium salts **17** with sodium borohydride and reaction of the 2-alkylthio-1,3-dithioles **19** with acid.[48,61] 1,3-Dithiolium salts **16** with the anions tetrafluoroborate, hexafluorophosphate, and perchlorate are well crystallizing salts, convenient for further reaction with tertiary aliphatic amines. Perchlorates must be handled with care. These salts are explosive and their handling in large quantities constitutes a potential hazard. Because at their high solubility and hygroscopic properties hydrogen sulfates are not convenient.

1.3 Dechalcogenization of 1,3-Dithiol-2-ones, -thiones and -selones to TTF by Trivalent Phosphorus Compounds (Method B)

After the conversion of 1,3-dithiolane-2-thiones with phosphites to tetrathioethylenes,[62] the formation of TTF by desulfurization of 1,3-dithiole-2-thiones with trivalent phosphorus compounds was also successful.[63] 1,3-Dithiole-2-thiones undergo the desulfurization reaction only when they are substituted by electron-withdrawing groups ($-COOR$, $-CF_3$, $-CN$),[63–66] by alkylthio groups,[28,67–69] by heterocycles,[48,68] or if they are benzo-annelated.[58,70] As trivalent phosphorus compounds trialkyl and triaryl phosphites as well as triphenylphosphine are convenient.[64,66] Often the yields of TTF are higher with 1,3-dithiol-2-ones or -selones than with 1,3-dithiole-2-thiones.[28,48,64,68,71] 1,3-Dithiole-2-thiones can easily be converted into 1,3-dithiol-2-ones by reaction with mercuric acetate in chloroform/glacial acetic acid[72] or into 1,3-dithiole-2-selones after alkylation and subsequent treatment with hydrogen selenide.[73]

1.4 Treatment of 1,3-Dithiolium Salts with Phosphoranes and Triethylamine (Method C)

1,3-Dithiol-2-ylidenephosphoranes **21** are prepared, as unstable compounds, by deprotonation of 1,3-dithiolylphosphonium salts **22** with butyllithium at −78 °C in tetrahydrofuran.[74–79] 1,3-Dithiolylphosphonium salts **22** are obtained in the case of alkyl

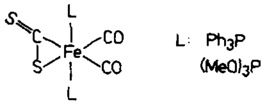


substituted, the unsubstituted, and benzo-annelated compounds by reaction of the 1,3-dithiolium salts **16** with a phosphine. Because 1,3-dithiolium salts **16** with electron-withdrawing substituents in 4- and 5-position can only be formed with difficulty, these 1,3-dithiolylphosphonium salts **22** are better synthesized by treatment of acetylenes with an adduct of carbon disulfide and a phosphine in acidic solution at −65°C in ether.[77,78,80]

The so prepared 1,3-dithiol-2-ylidenephosphoranes **21** react in the presence of triethylamine with 1,3-dithiolium salts **16** to form TTF.[75,77,81] This method has the great advantage that unsymmetrical TTF derivatives can be prepared. Other methods for the synthesis of unsymmetrical TTF by coupling two different 1,3-dithiole derivatives require the separation from symmetrical co-products by fractional recrystallization[47,82,83] or chromatography.[84,85]

1.5 TTF by Reaction of Carbon Disulfide with Acetylenes (Methods D and E)

The reaction between the adduct of carbon disulfide and tributylphosphine with methyl propiolate at −30 °C in tetrahydrofuran in the absence of acid and with excess carbon disulfide gives the corresponding TTF and not the 1,3-dithiolylphosphonium salt **22**.[34] Electron-deficient acetylenes form with carbon disulfide, activated by the iron complex **23**, TTF in moderate yield (25–30%).[86,87]



23

Acetylenes with electron-withdrawing substituents and carbon disulfide react at 100 °C in a sealed tube to form TTF derivatives in very low yield (2%).[63] The preparation of TTF in high yield is achieved by carrying out the reaction under high pressure (5000–6000 atm)[88–90] or in the presence of strong acids (trifluoroacetic acid).[63,91]

1.6 TTF by Treatment of 2-Alkylthio-, 2-Arylthio- and 2-Alkylseleno-1,3-dithiolium Salts with Trivalent Phosphorus Compounds (Method F)

TTF are generated by treatment of 2-alkylthio- or 2-arylthio-1,3-dithiolium salts with triethyl phosphite or triphenylphosphine in higher yields and with short reaction time than by treatment of the corresponding 1,3-dithiole-2-thiones. By use of 2-alkylseleno-1,3-dithiolium salts the highest yields are obtained. In this case also tributylphosphine or hexamethylphosphorous triamide can be used as trivalent phosphorus compounds.[92]

1.7. TTF by Treatment of 2-Methylthio-1,3-dithiolium Salts with Zinc and Bromine (Method G)

In a convenient way and with easily varied substituents (alkyl, aryl, benzo) TTF are prepared by the treatment of 2-methylthio-1,3-dithiolium salts **17** (R = Me) with zinc dust in ethanol in the presence of an oxidizing agent or an electrophilic reagent. Suitable oxidizing agents are bromine, iodine, peracetic acid, lead dioxide, or hydrogen peroxide, and electrophilic reagents, proton acids, methyl iodide, or dimethyl sulfate. The yield reaches values between 35 and 65%.[93]

1.8. *TTF by Reaction of 1,2-Dimercapto Compounds with Tetrachloroethylene (Method H)*

By treating 1,2-dimercaptobenzene derivatives **15** with tetrachloroethylene under basic conditions (*N,N*-diisopropylethylamine, triethylamine, pyridine, *N,N*-dimethylformamide) one can obtain TTF in modest yields (5–35%).[47,94] This method was already used in 1926 for the synthesis of the first tetrathiafulvalene.[95]

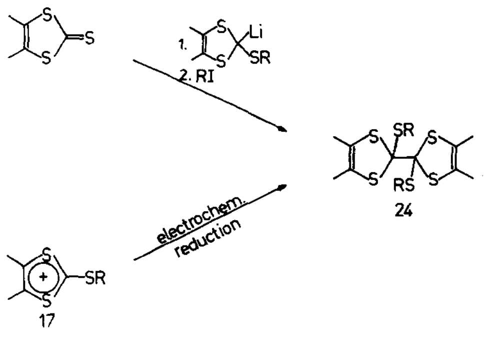
1.9 *Miscellaneous Methods*

A photochemical method for the synthesis of TTF is the irradiation of 1,3-dithiole-2-thiones with u.v. light in benzene.[96] The yields are modest (5–25%), better in the prescence of triethylamine or triethyl phosphite.[96] Only phenyl substituted and benzo-annelated compounds react, but cycloalkyl substituted thiones are inactive and donor or acceptor substituted derivatives are decomposed in an obscure way.

The irradiation of 1,3-dithiole-2-thiones in the presence of hexabutyldistannane produces the corresponding TTF in appreciably higher yields (50–80%). The method is also generally usable for the preparation of TTF substituted either by electron-donating or electron-withdrawing groups (method M).[97,98]

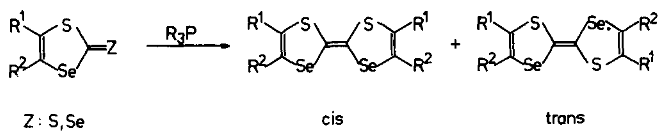
In a one-step synthesis TTF are afforded directly from 1,3-dithiole-2-thiones, substituted with electron-donating or electron-withdrawing groups, in 10–60% yield by heating with dicobalt octacarbonyl or triiron dodecacarbonyl in benzene or toluene solutions (method I).[36,64,99]

Thermolysis of the orthothiooxalates **24** in carbon tetrachloride gives TTF in high yield. [39,100] The addition of catalytic amounts of *p*-toluenesulfonic acid accelerates the reaction.[100] The orthothiooxalates **24** are formed by the electrochemical reduction of the 2-alkylthio-1,3-dithiolium salts **17**[39,101,102] or by treatment of 1,3-dithiole-2-thiones with 2-lithio-2-alkylthio-1,3-dithioles and alkylation of the formed intermediates. The 2-lithio-2-alkylthio-1,3-dithioles are prepared by deprotonation of 2-alkylthio-1,3-dithioles with butyllithium at − 78 °C in tetrahydrofuran.[103] This last method for the synthesis of orthothiooxalates **24** allows the formation of unsymmetrical TTF in their pure form (method K). Thermolysis of 2-alkoxy-1,3-dithioles also produces TTF.[104] The yield increases if the thermolysis is performed in benzene in the presence of trichloroacetic acid.[105] Electrochemical oxidation of 1,3-dithioles **25** in acetonitrile, in the presence of pyridine, provides TTF directly (method L).[106] TTF data are summarized in Table 5.



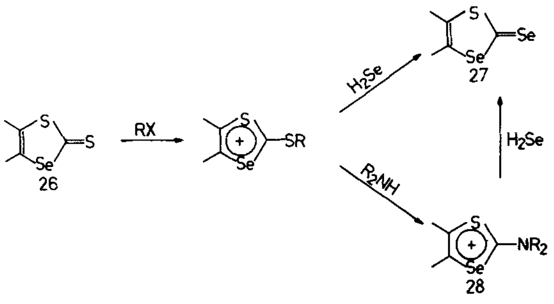
2. SYNTHESIS OF DISELENADITHIAFULVALENES (DSDTF), (1,3-THIASELENOLE-2-THIONES AND -SELONES)

The synthesis of symmetrical DSDTF is successful only by treatment of 1,3-thiaselenole-2-thiones or -selones with trivalent phosphorus compounds (trimethyl or triethyl phosphite, triphenylphosphine). The coupling reaction affords a *cis*- and *trans*-mixture of isomers.

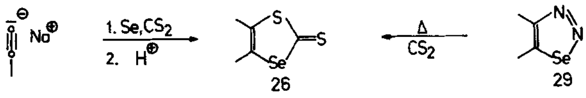


This mixture cannot be separated at all.[107,108] The existence of both isomers is proved by ^{1}H NMR spectra.[28,73,107,109]

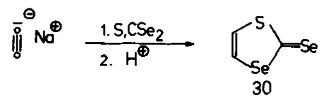
Among the unsubstituted compounds the reaction works only with 1,3-thiaselenole-2-selone.[107,108] Selones normally give higher yields than the corresponding thiones.[28,110] Therefore 1,3-thiaselenole-2-thiones **26** are converted into the 1,3-thiaselenole-2-selones **27**. This occurs in the case of the methyl substituted compound **26** by alkylation and treatment of the formed thiaselenolium salt with hydrogen selenide,[73] or in the case of cycloalkyl substituted and benzo-annelated derivatives[110] as well as unsubstituted 1,3-thiaselenole-2-thione[108] by conversion to a 2-amino-1,3-thiaselenolium salt **28** and following treatment with hydrogen selenide.[108,110] Methyl-, phenyl- and unsubstituted 1,3-thiaselenole-2-thione **26** is prepared in a simple one-step synthesis, adding selenium and carbon disulfide to the corresponding acetylide.[111,112]



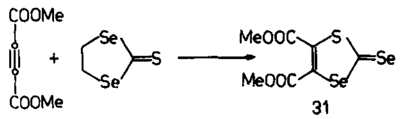
Thermolysis of the corresponding 1,2,3-selenadiazoles **29** in excess carbon disulfide affords the unsubstituted,[108] the cycloalkyl substituted[28,110,113] and the benzo-annelated[110]



1,3-thiaselenole-2-thione **26**. The 1,3-thiaselenole-2-selones **27** can also be obtained directly. The unsubstitued compound **30** is formed in low yield (8%) from sodium acetylide, sulfur and carbon diselenide.[112]



Treatment of 1,3-diselenolane-2-thione with dimethyl acetylenedicarboxylate gives the corresponding selone ester **31** in good yield (70%).[108,114] DSDTF and their data are summarized in Table 6.



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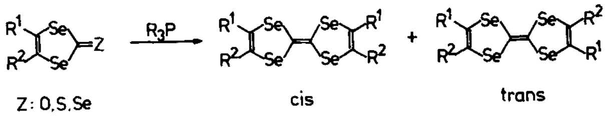
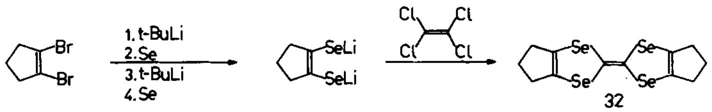
3. SYNTHESIS OF TETRASELENAFULVALENES (TSF)

TSF are obtained by coupling of 1,3-diselenole-2-thiones, -selones, or -ones with trivalent phosphorus compounds.



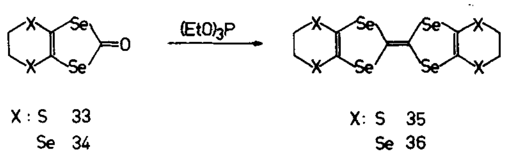
If differently substituted 1,3-diselenole derivatives are used, a mixture of cis/trans isomers is formed. Only in one case could this mixture be separated on the basis of solubility differences of the isomers.[115]

Only tetrakis(trimethylsilyl)tetraselenafulvalene has been synthesized by reaction under high pressure (5000–6000 atm) between bis(trimethylsilyl)acetylene and carbon diselenide in moderate yield (20%).[90] Hexamethylenetetraselenafulvalene **32** was obtained by a synthesis analogous to that of the tetratellurafulvalenes.[116]



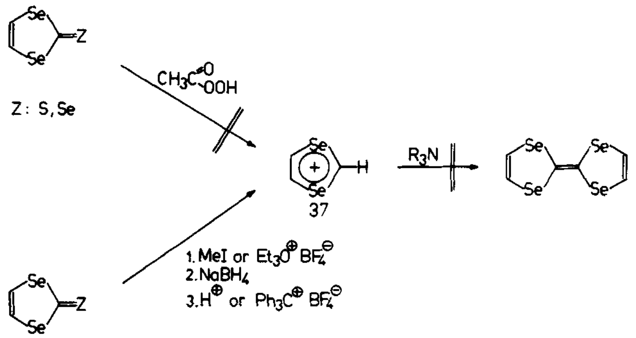
32

The 1,3-diselenole-2-selones give mostly higher yields of TSF than the corresponding 1,3-diselenole-2-thiones.[71,117] By using 1,3-diselenole-2-thiones an unexpected selenium-sulfur scrambling can appear, so that triselenathiafulvalenes are formed as by-products.[117] The synthesis of bis(ethylenedithio)- and bis(ethylenediseleno)tetraselenafulvalene **35** resp. **36** is successful only by using 4,5-ethylenedithio- or 4,5-ethylenediseleno-1,3-diselenol-2-one **33** resp. **34**.[68,118]



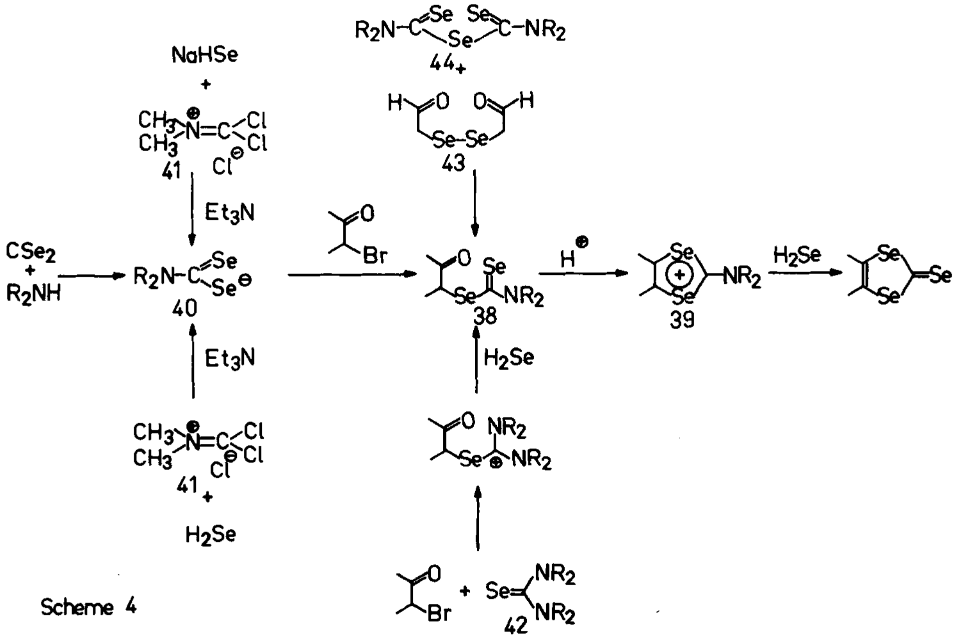
The corresponding selones do not react with triethyl phosphite.

Contrary to TTF synthesis, an analogous formation of TSF by oxidation of 1,3-diselenole-2-thiones or -selones with peracids and the following reaction with trialkylamines could not be realized.[71] The oxidation of 1,3-diselenole-2-thiones or -selones fails to give the desired 1,3-diselenolium salts **37**.[71,119,120] If they are available by alkylation of 1,3-diselenole-2-thiones or -selones, reduction with sodium borohydride and treatment with tetrafluoroboric acid[121] or trityl tetrafluoroborate,[122] the reaction of **37** with trialkylamines provides only elemental selenium as precipitate.[71]



3.1 1,3-Diselenole-2-selones as Starting Materials for TSF

The required 1,3-diselenole-2-selones can be prepared using various methods (Scheme 4).



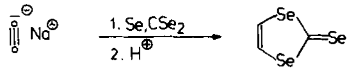
Scheme 4

Analogous to 1,3-dithiole-2-thiones,[21-23] 1,3-diselenole-2-selones are synthesized by ring closure of *β*-keto-*N*,*N*-dialkyldiselenocarbamates **38** with concentrated sulfuric acid at room temperature and subsequent treatment of the formed 2-(*N*,*N*-dialkylamino)-1,3-

diselenolium salts **39** with hydrogen selenide in 70% methanol.[120,123] Before reaction with hydrogen selenide, the 2-(*N*,*N*-dialkylamino)-1,3-diselenolium hydrogen sulfates **39** are converted to well crystallizing, but explosive perchlorates.[120,123,124] Less dangerous is the handling of tetrafluoroborates[125] or hexafluorophosphates.[126,127]

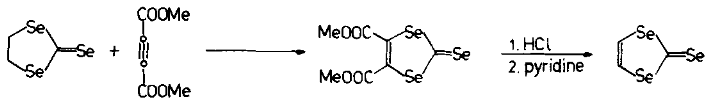
Alkyl,[120,123] aryl,[120] and aralkyl substituted[124] β-keto-*N*,*N*-dialkyldiselenocarbamates **38** are generated by treatment of the corresponding α-bromo ketones with *N*,*N*-dialkyldiselenocarbamates **40**. In the synthesis of alkyl derivatives a convenient solvent is methylene chloride[120,128,129] or *N*,*N*-dimethylformamide[126] and for aralkyl substituted compounds methanol.[130]

The *N*,*N*-dialkyldiselenocarbamate **40** is prepared by the reaction of carbon diselenide with a dialkylamine (*e.g.* piperidine, morpholine, pyrrolidine).[120,131] Since carbon diselenide is an extremly fetid reagent and only produced in 30% yield via the rection of methylene chloride with selenium at 600 °C,[132] it is better to treat hydrogen selenide with dichloromethylene-*N*,*N*-dimethylammonium chloride **41**[133] in the presence of triethylamine[129,134] or piperidine.[128] The disadvantages of handling gaseous hydrogen selenide are avoided by the use of sodium hydrogen selenide, which can be generated by reducing black selenium with sodium borohydride in the reaction mixture.[126] Synthesis of β-keto-*N*,*N*-dialkyldiselenocarbamates **38** without use of carbon diselenide is possible by reaction of *N*,*N*,*N*′,*N*′-tetramethylselenourea **42** with α-bromo ketones, followed by treatment with hydrogen selenide.[135] The disadvantage of this method is that only fair yields of **38** are obtainable. The reaction between the corresponding diselenide **43** and bis(*N*,*N*-dialkylselenocarbamoyl) selenides **44** in the presence of *p*-toluenesulfonic acid in chloroform leads to the β-formyl-*N*,*N*-dialkyldiselenocarbamates **38**, which permit access to the unsubstituted 1,3-diselenole-2-selone.[127] The unsubstituted and 4-phenyl

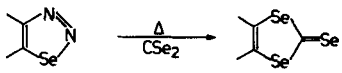


substituted 1,3-diselenole-2-selone is prepared more easily in analogy to 1,3-dithiole-2-thione[33] by addition of selenium and carbon diselenide to the corresponding sodium acetylides[112,112a]

In a multistep synthesis the parent compound is obtained, also in analogy to 1,3-dithiole-2-thione,[34] in high yield (every step over 60%) by reaction of 1,3-diselenolane-2-selone with dimethyl acetylenedicarboxylate, followed by hydrolysis and decarboxylation.[136]



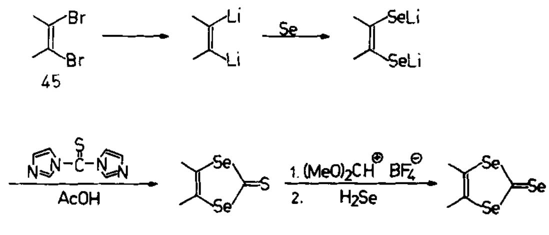
Cycloalkyl substituted[28,137] and benzo-annelated[138] 1,3-diselenole-2-selones are formed in moderate (10–35%) resp. good (70%) yields by thermolysis of the corresponding 1,2,3-selenadiazoles **29** in presence of excess carbon diselenide. Thermolysis of 1,2,3-selenadiazoles **29** takes place under appreciably milder conditions (reflux in toluene, xylene, carbon diselenide) than the thermolysis of 1,2,3-thiadiazoles **14**. In the presence of

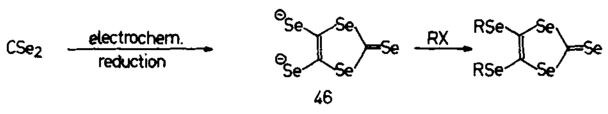


29

potassium *t*-butoxide thermolysis of the unsubstituted 1,2,3-selenadiazole **29** already occurs at 0 °C and gives 1,3-diselenole-2-selone in 40% yield.[122]

Benzo-annelated[139] and heterocyclo substituted[48–50] 1,3-diselenole-2-selones are prepared in analogy to the corresponding sulfur compounds[47–50] from the 1,2-dibromo derivatives **45**. These are lithiated with *t*-butyllithium or via a *o*-phenylenemercury compound[140] with lithium, then treated with selenium powder and afterwards the corresponding 1,3-diselenole-2-thione is formed with thiocarbonyldiimidazole in glacial acetic acid/tetrahydrofuran. By alkylation of the thione and reaction with hydrogen selenide the 1,3-diselenole-2-selone is obtained. Electrochemical reduction of carbon diselenide at 40 °C provides the 4,5-diselenolate-1,3-diselenole-2-selone **46**, which can be alkylated with alkylating agents.[118] The same product is also afforded by reduction with potassium naphthalide in tetrahydrofuran.[118]

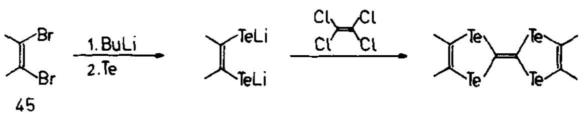




TSF and their data are summarized in Table 7.

4. SYNTHESIS OF TETRATELLURAFULVALENES (TTeF)

Hitherto the only known method for the synthesis of tetratellurafulvalenes is the following: 1,2-Dibromo derivatives **45** are lithiated with *t*-butyllithium, then treated with tellurium powder and finally with tetrachloroethylene.[49,50,141–143] Yields vary between 10 and 75%. TTeF and their data are summarized in Table 8.



5. SYNTHESIS OF CONJUGATED TETRATHIA- AND TETRASELENAFULVALENES

Conjugated tetrathia- and tetraselenafulvalenes are stronger donors than the corresponding tetrathia- and tetraselenafulvalenes. With increasing extension of the con-

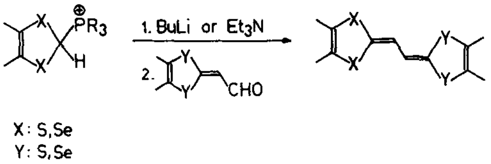
TABLE 1

Oxidation potentials of vinylogous tetrathia- and tetraselenafulvalenes and their parent compounds[144,145] in acetonitrile (vs. Ag/AgCl electrode, 0.1 M Et_4NClO_4)

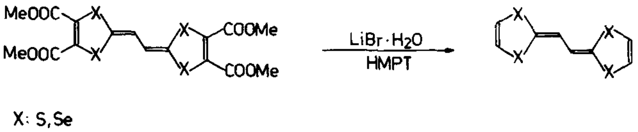
n	X	E_1^{Ox} (V)	E_2^{Ox} (V)	ΔE (V)
1	S	0.34	0.71	0.37
2	S	0.20	0.36	0.16
3	S	0.22		
1	Se	0.49	0.77	0.28
2	Se	0.33	0.47	0.14

jugated electron system the oxidation potential becomes smaller than that of the parent compound. By the same token the Coulomb repulsion between the charges of the dication is decreased. This is apparent in the decrease of the difference between the two oxidation potentials ($E_2 - E_1$). In the tetrathiafulvalene derivative with three double bonds the difference is so small that only one wave, representing a two-electron oxidation, appears (Table 1).[144]

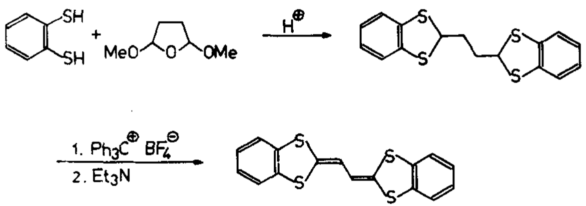
Essentially the synthesis of the ethanediylidene derivatives is based on the Wittig-type reaction of a phosphorane with the appropriate aldehyde.[79,145]



By this reaction it is possible to obtain unsymmetrically substituted derivatives. The unsubstituted compound is formed by decarbomethoxylation of the corresponding tetraester with lithium bromide monohydrate in hexamethylphosphoramide at 160 °C.[79,145]

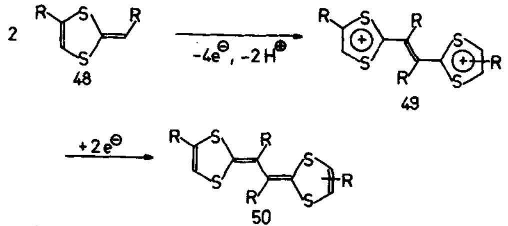


The benzo-annelated compound **47** is prepared by treatment of 1,2-benzenedithiol with 2,5-dimethoxytetrahydrofuran in acidic solution, followed by hydride abstraction



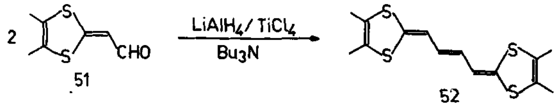
47

and deprotonation.[146,147] The oxidative dimerization of 1,4-dithiafulvenes **48** with *p*-benzoquinones provides the corresponding dications **49**, which can be reduced to the ethanediylidene derivatives **50** with zinc dust or mercury.[148]

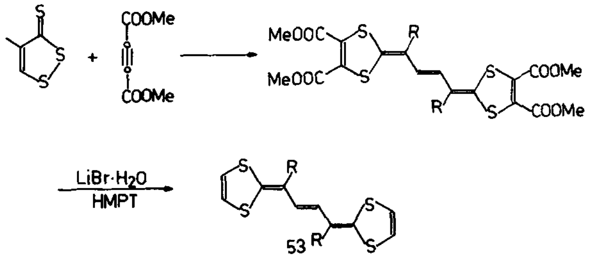


R	C_6H_5	$4\text{-}ClC_6H_4$	$4\text{-}MeC_6H_4$	$4\text{-}MeOC_6H_4$

The unsubstituted and the benzo-annelated compound in the series of 1,4-butenediylidene derivatives **52** are obtained by reduction of the corresponding 2-formylmethylene-1,3-dithiole **51** with lithium aluminium hydride in the presence of titanium tetrachloride and tributylamine in tetrahydrofuran.[144]

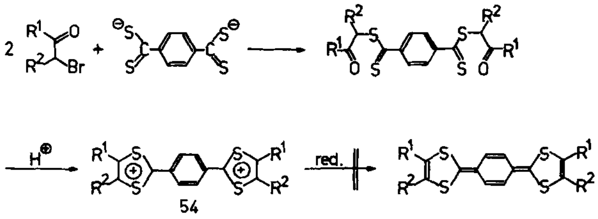


The unsubstituted compound **53** (R = H) is also formed by treatment of 1,2-dithiole-3-thione with dimethyl acetylenedicarboxylate in benzene, followed by decarbomethoxylation with lithium bromide monohydrate in hexamethylphosphoramide.[144]



R : H,Ph

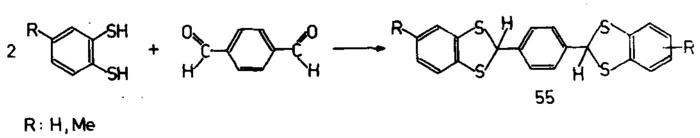
The 1,3-dithiolylidene units have also been connected by a *p*-benzoquinoid system, but these compounds are rather unstable. Both the tetramethyl[149] and the diphenyl derivative[150] **54** ($R^1 = R^2 =$ Me resp. $R^1 =$ Ph, $R^2 =$ H) could be isolated as dications. For the unsubstituted compound **54** ($R^1 = R^2 =$ H) no details have been reported.[151]



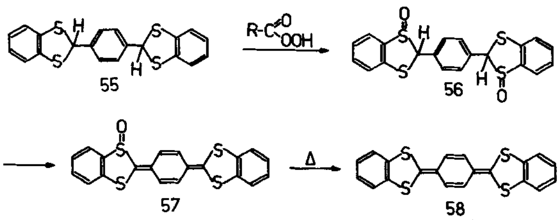
$R^1 = R^2$: H, Me
R^1 : Ph R^2 : H

Polarographic reduction or reduction with zinc dust only lead to unstable products. With lithium iodide the dication of the diphenyl derivative could be converted into a stable iodine complex.[150]

Benzo-annelated derivatives are formed by reaction of the corresponding 1,2-dimercapto compounds with terephthaldehyde.

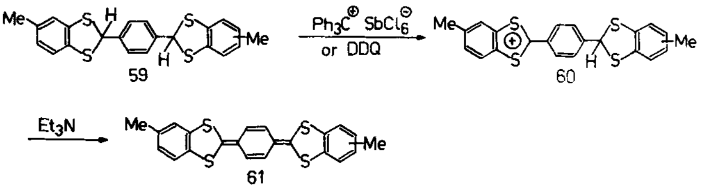


The unsubstituted derivative 55 (R = H) could not be dehydrogenated with chloranil or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.[152,153] Instead an unusual method is used. The dihydro compound 55 is oxidized with *m*-chloroperbenzoic acid to the disulfoxide



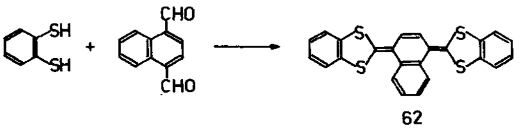
56, converted to the monosulfoxide 57 with diazabicyclononene and pyridine the pyrolysis of which gives cyclohexa-2,5-diene-1,4-diylidenebis-1,3-benzodithiole 58.[152,153]

The dimethyl derivative 61 could be synthesized by treatment of the corresponding

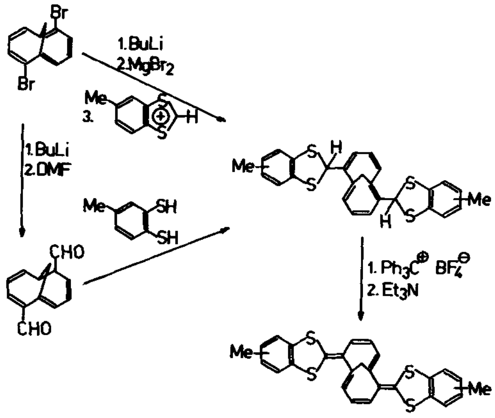


dihydro compound with trityl hexachloroantimonate or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to form the monocation 60, followed by deprotonation with triethylamine.[154]

Both the unsubstituted and the dimethyl derivative 58 resp. 61 are slightly air sensitive and decompose. In the same way the 1,4-naphthoquinonoid compound 62 is formed.[155]

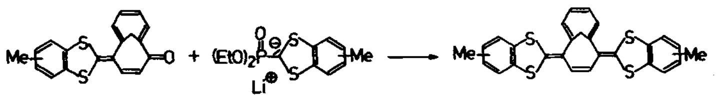


In an analogous manner the bicyclic bridged tetrathiafulvalene 63 can be prepared as a diastereomeric mixture.[156]



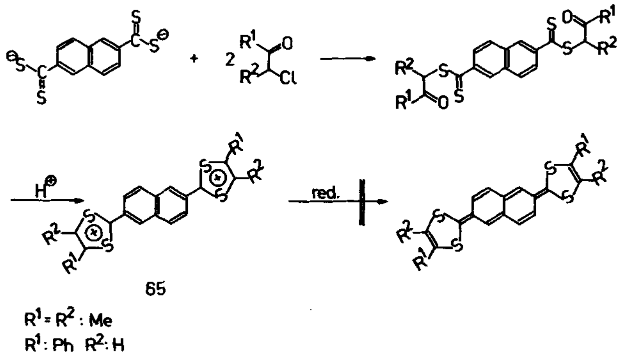
63

Via a Wittig-Horner reaction the structurally isomeric tetrathiafulvalene 64 is formed.[156]



64

A coupling to a 2,6-naphthoquinonoid system was also successful.[157,158]



65

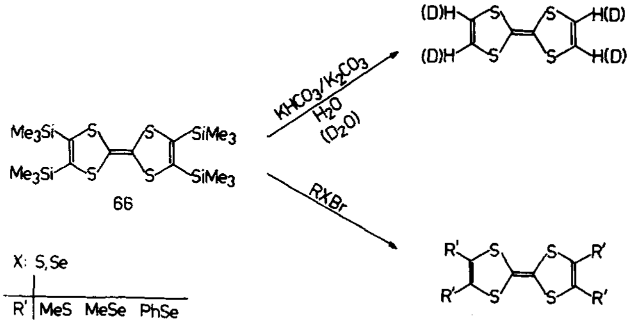
What could be isolated, like in the case of the corresponding benzoquinonoid derivative 54,[149] were only the dications 65. These form stable complexes with lithium iodide. The quinonoid-bridged tetrathiafulvalene derivatives are also stronger donors than the corresponding TTF with only one central ethylene bridge. The two reversible one-electron transitions in TTF are changed to a reversible two-electron transition in quinonoid systems.[156] Vinylogous TTF and TSF and their data are summarized in Table 9.

6. PROPERTIES OF TETRATHIA-, TETRASELENA- AND TETRATELLURAFULVALENES

6.1. *Conversion of Tetrathia- and Tetraselenafulvalene Derivatives*

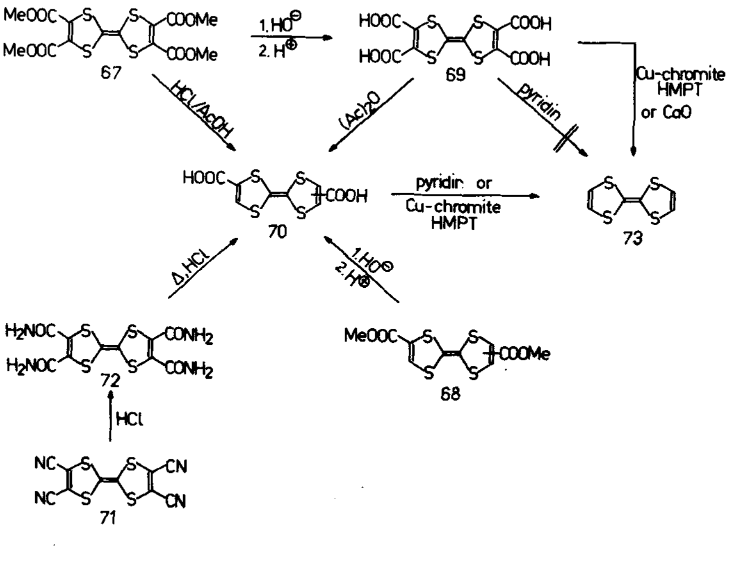
The tetrathia- and tetraselenafulvalene moiety is rather stable under basic and weakly acidic conditions so that a conversion of substituents can be accomplished without destroying the tetrathia- and tetraselenafulvalene structure.

In ethanol/tetrahydrofuran (1:1) at room temperature with an aqueous buffer solution from potassium carbonate and potassium hydrogen carbonate the trimethylsilyl groups of tetrakis(trimethylsilyl)tetrathiafulvalene **66** are readily replaced by hydrogen.



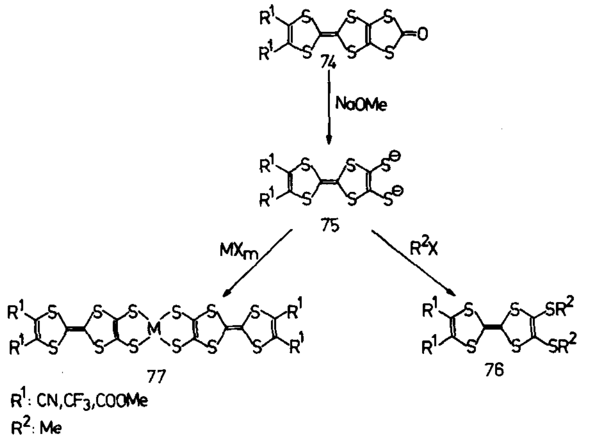
Deuterated solvents (D_2O, EtOD) under the same conditions afford deuterated tetrathiafulvalene. With sulfenyl or selenyl bromides the corresponding tetrakis(sulfenyl)- or tetrakis(selenyl)tetrathiafulvalenes are obtained.[90]

The tetrathiafulvalene tetraester **67** and the diester **68** can be hydrolyzed in aqueous or ethanolic alkaline solution[34,65,66,91] as well as in half-concentrated hydrochloric acid/



glacial acetic acid[66] to the corresponding tetraacid **69** or diacid **70**, respectively, where the hydrolysis is accompanied by decarboxylation under acidic conditions. Hydrolysis of tetracyanotetrathiafulvalene **71** in concentrated hydrochloric acid at room temperature gives tetrathiafulvalene tetraamide **72**. Hydrolysis with reflux does not provide the amide **72**, but generates the diacid **70** by simultaneous decarboxylation.[66] The diacid **70** is also formed upon heating of the tetraacid **69** in acetic anhydride.[66] The diacid **70** decarboxylates in pyridine at 250 °C in a sealed tube to the parent tetrathiafulvalene **73**.[34,66] Under these conditions the tetraacid **69** does not decarboxylate.[65] The decarboxylation of the diacid **70** as well as of the tetraacid **69** in hexamethylphosphoramide at 150 °C in the presence of copper chromite gives the parent tetrathiafulvalene **73**. Also copper(II) sulfate or copper powder in quinoline induces the decarboxylation of acid derivatives.[159] The tetraacid **69** can be decarboxylated by heating at 300 °C in the presence of calcium oxide.[91]

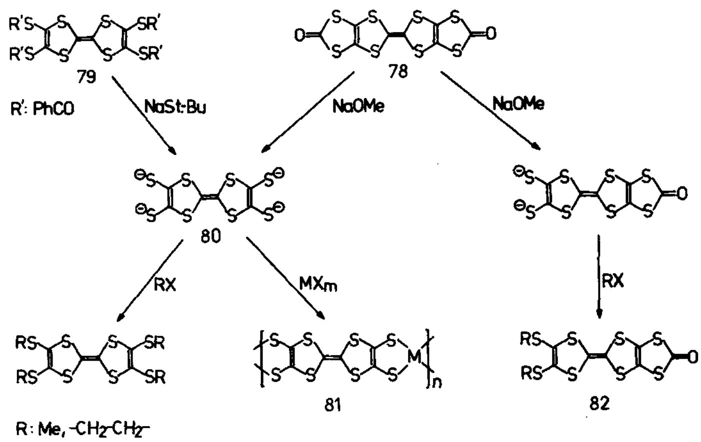
1,3-Dithiole-2-ono-annelated TTF **74** are degraded by strong bases like sodium methoxide or methyllithium.[33,160,161]

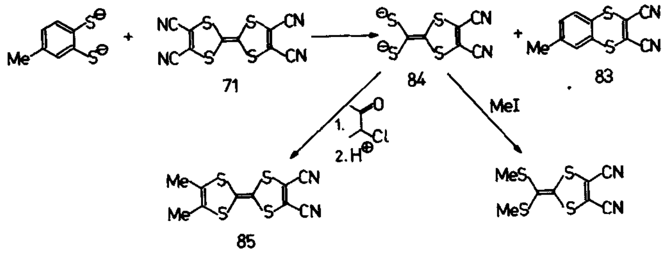


The dithiolate salts **75** so formed can be converted with alkylating agents to different substituted tetrathiafulvalenes **76**[161] and with transition metal salts to the corresponding metal dithiolene complexes **77**.[162]

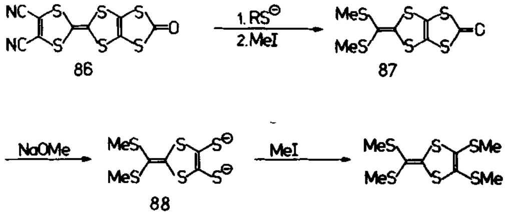
In the same manner bis(1,3-dithiole-2-ono)tetrathiafulvalene **78**[40,44,162-164] and tetrakis(benzoylthio)tetrathiafulvalene **79**[165] are cleaved. The air-sensitive tetrathiolate salt **80** obtained affords on addition of alkylating agents the known TTF[40,163,166] and with transition metal salts the polymeric dithiolene complexes **81**.[44,162,164] When only two equivalents of base are used and subsequently treated with methyl iodide, the half-opened dimethylthio derivative **82** is formed.[163]

The nucleophilic attack of the salt of 3,4-toluenedithiol upon tetracyanotetrathiafulvalene **71** provides 2,3-dicyano-5,6-toluo-1,4-dithiene **83** and the air-sensitive geminal dithiolate intermediate **84** which can be converted with methyl iodide or 3-chloro-2-butanone and subsequently with concentrated sulfuric acid to a new tetrathiafulvalene derivative **85**. Also alkane-, arene-, acylthiols, -selenol and -tellurol salts react with tetracyanotetrathiafulvalene **71** in an analogous manner to give the geminal dithiolate intermediate **84**. Tetracyanotetraselenafulvalene reacts in a similar fashion.[167]



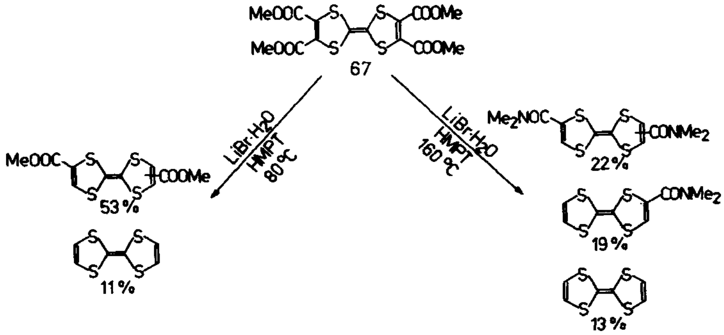


The reaction of the unsymmetrically substituted tetrathiafulvalene **86** with thiol salts leads to attack preferentially at the cyano substituted double bond. After alkylation with



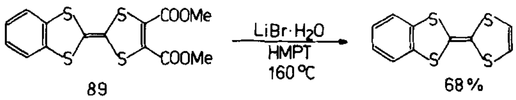
methyl iodide the product **87** formed can be cleaved at the dithiocarbonate group with a stronger base (NaOMe, MeLi) to give a 1,2-dithiolate intermediate **88** which is then alkylated.[167]

Heating of the tetraester **67** with excess lithium bromide monohydrate in hexam-

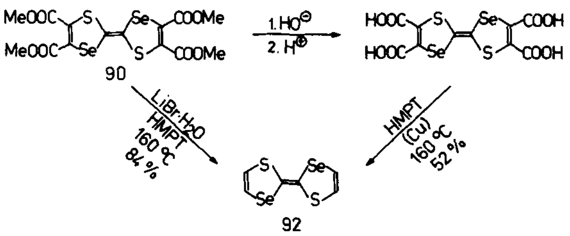


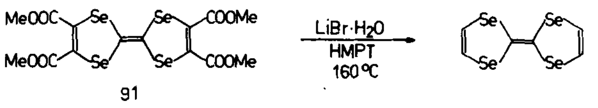
ethylphosphoramide at various temperatures affords the parent tetrathiafulvalene and other products.[159]

More effective is the treatment of the unsymmetrical tetrathiafulvalene diester **89** with lithium bromide monohydrate in hexamethylphosphoramide.[84]



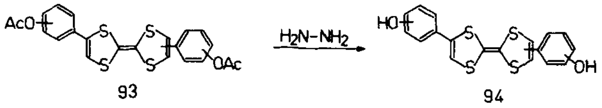
Under the same conditions the *sym*-diselenadithiafulvalene tetraester **90**[108] and tetraselenafulvalene tetraester **91**[168] decarbomethoxylate, too.





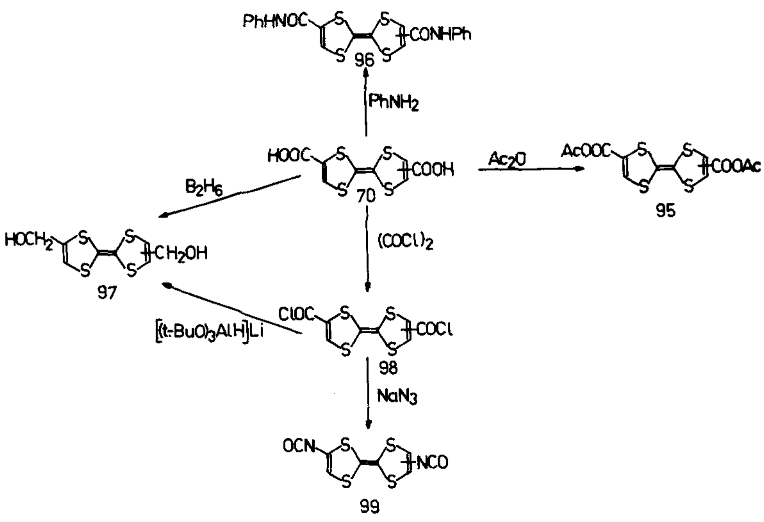
The *sym*-diselenadithiafulvalene **92** is also formed by hydrolysis of *sym*-diselenadithiafulvalene tetraester **90** in alkaline solution, followed by decarboxylation in hexamethylphosphoramide in the presence of copper bronze.[108,114]

For the hydrolysis of the substituted aryltetrathiafulvalenes **93** hydrazine in methanol is a convenient reagent.[65,169]

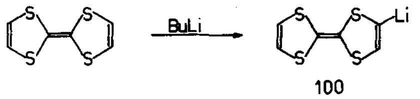


After treatment with long-chain acid chlorides in pyridine the 2,6(7)-bis(*p*-hydroxyphenyl)tetrathiafulvalene **94** constitutes a TTF with liquid crystal properties.[170,171] The tetrathiafulvalene diacid **70** can be converted to various other acid derivatives.

With acetic anhydride in tetrahydrofuran the bis-anhydride **95** is formed,[65] with aniline in dimethylformamide at 70 °C, with diphenyl phosphite-pyridine as dehydrating reagent, the bis-anilide **96**,[65] and with diborane in diglyme the bis(hydroxymethyl)tetrathiafulvalene **97**[65] is obtained. The acid function is converted to the acid chloride **98** with oxalyl chloride in methylene chloride[172] or in benzene/acetonitrile.[173] The tetrathiafulvalenedicarbonyl chlorides **98** yield, with activated sodium azide in benzene or toluene, in a Curtius reaction the corresponding isocyanates **99**.[172,173] Tetrathiafulvalene- dicarbonyl chlorides **98** are reduced with lithium tri-*t*-butoxyaluminium hydride in tetrahydrofuran to bis(hydroxymethyl)tetrathiafulvalenes **97**.[172]

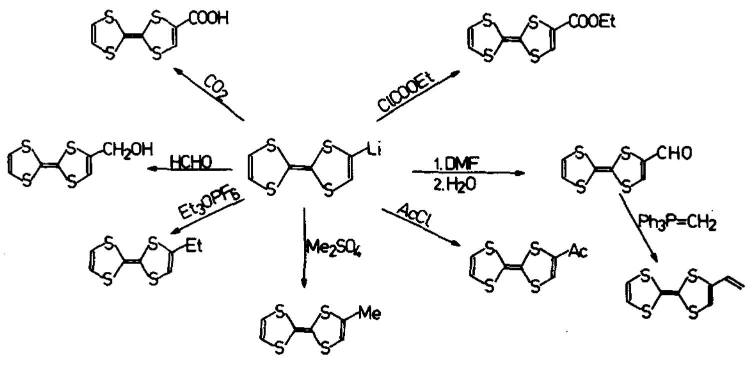


The parent tetrathiafulvalene and substituted TTF are lithiated by butyllithium or lithium diisopropylamide in ether at −70 °C.

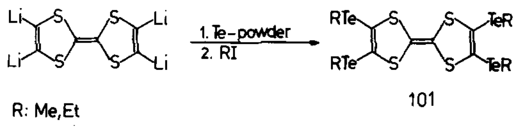


100

Tetrathiafulvalenyllithium **100** is very reactive and can be treated with a variety of reagents to produce monosubstituted TTF in yields of 30–70%.[174,175] This reaction constitutes a general method for the synthesis of unsymmetrically substituted TTF.



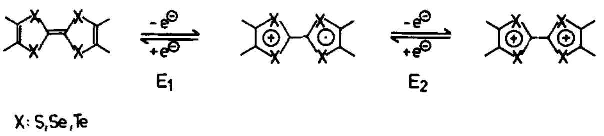
Multilithiated TTF are formed when the lithiation is carried out at −20 °C or when an excess of the lithiation reagent is used. The treatment of multilithiated TTF with reagents provides multisubstituted TTF. Thus it is possible to synthesize alkyltelluro-tetrathiafulvalenes **101**.[176]



101

6.2 *Redox Reactions and Spectroscopic Behaviour of Tetrathia-, Tetraselena- and Tetratellurafulvalenes*

Tetrathia-, tetraselena-, and tetratellurafulvalenes are good electron donors which can be oxidized in two successive one-electron steps to their mono- and dications.



Polarographically it has been proven that these electron transfers are reversible for the tetrathia-[58,177] as well as for the tetraselena-[178] and tetratellurafulvalenes.[141]

The half-wave oxidation potentials E_1^{Ox} and E_2^{Ox} show that the donor strength decreases from tetrathiafulvalene to the corresponding tetraselenafulvalene and increases again for the corresponding tetratellurafulvalene (Table 2).

This is caused by two factors which have opposite effects. The π-orbital interaction between the carbon framework and the heteroatoms decreases as a result of increasing atom size in the series S, Se, Te. Therefore in this series the resonance stabilization of the positive charge after removal of an electron also decreases and higher energy is required for the removal of this electron. On the other hand the ionization potential decreases in the series S, Se, Te. Hence the ionization of the TTF should occur primarily from the π-bonded network and in the TTeF from the tellurium lone pairs.[141,142]

TABLE 2

Oxidation potentials of substituted tetrathia-, tetraselena-, and tetratellurafulvalenes vs. sce.[141,142]

	E_1^{Ox} (V)	E_2^{Ox} (V)	ΔE (V)
TMTTF	0.24[a]	0.73	0.49
TMTSF	0.42[a]	0.81	0.39
HMTTeF	0.40[a]	0.60	0.29
DBTTF	0.71[b]	1.14	0.43
DBTSF	0.78[b]	1.17	0.39
DBTTeF	0.71[b]	1.05	0.34

[a] benzonitrile, Bu_4NAsF_6; TMTTF and HMTTF as well as TMTSF and HMTSF have practically identical redox properties.[28,179]

[b] methylene chloride, 0.2 M Bu_4NBF_4; TMTTF, HMTTF: tetramethyl-, hexamethylenetetrathiafulvalene, resp. TMTSF, HMTSF: tetramethyl-, hexamethylenetetraselenafulvalene, resp. HMTTeF: hexamethylenetetratellurafulvalene. DBTTF, DBTSF, DBTTeF: dibenzotetrathia-, dibenzotetraselena-, dibenzotetratellurafulvalene, resp.

The donor strength is also influenced by substituents. It is increased by electron-donating and lowered by electron-withdrawing substituents. In diaryl substituted TTF the first half-wave potential correlates with the Hammett values, where the σ_p^+-values understandably provide a better correlation than the σ_p-values (Figure 1).[180]

After removal of an electron the radical cations or dications formed are stable and can be isolated as salts in substance in most cases. The formation constants K of the radical cations are calculable from the redox potentials.[181]

$$\log K = \frac{E_2^{Ox} - E_1^{Ox}}{0.059}$$

The radical cations give ESR spectra the resolution of which depends on the solvents and the formation conditions. The line width increases from tetrathiafulvalene[58,177,182–187] to tetraselenafulvalene radical cations.[188,189] The low solubility of the TTeF has so far thwarted the generation of radical cations and the recording of their ESR spectra.[141] The oxidation of TTF[190,191] and TSF[191,192] can take place electrochemically. With a low current single crystals are generated.[192]

Likewise the application of oxidation agents affords radical cations or dications. TTF are oxidized *e.g.* with halogens,[58,182,193,194] thiocyanogen,[195] metal salts,[196–198] hydrogen peroxide,[199,200] aryldiazonium salts,[201,202] lead(IV) acetate,[58] lead(IV) oxide,[180,203] or halocarbons in the presence of light[204,205] and TSF *e.g.* with iodine[115,206] or lead(IV) oxide.[124] The radical cations are also formed in comproportionation reactions between the dications and the parent tetrathia- or tetraselenafulvalenes, resp.[124,180,203]

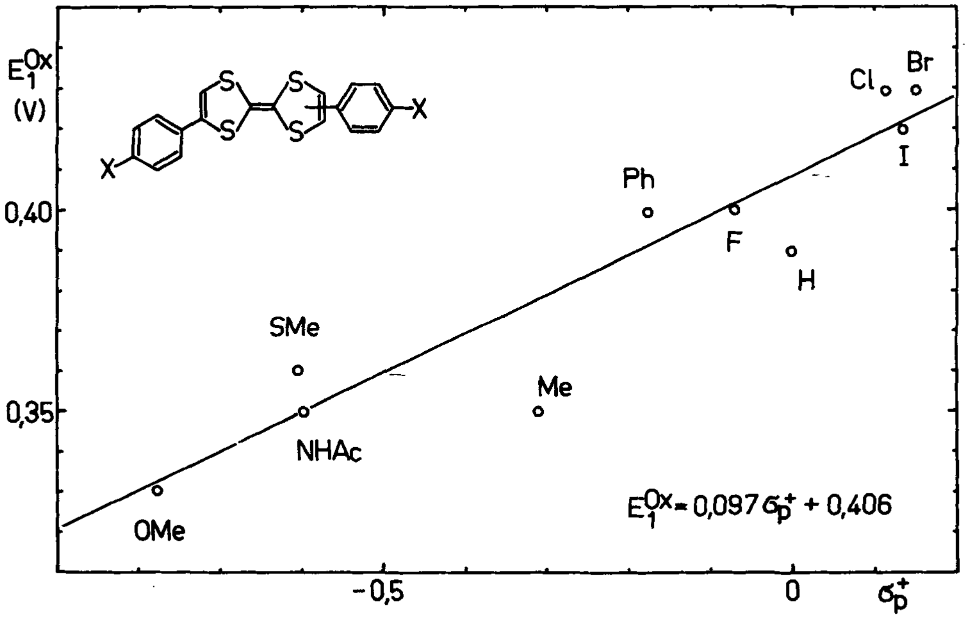
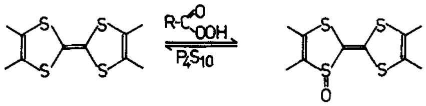


FIGURE 1. Relation of half-wave potentials vs. sce for oxidation of 2,6(7)-diaryl substituted TTF in methanol/benzene (4:1, v:v) to Hammett substituent constants.

Reduction of the monocations and dications with sodium bisulfite regenerates the corresponding TTF or TSF.[115,182] When TTF are oxidized with *m*-chloroperbenzoic acid the corresponding tetrathiafulvalene *S*-oxides are formed.[207,208] The tetrathiafulvalene *S*-oxides **102** are also formed under the influence of air oxygen on TTF.[208] Therefore the



102

TTF should be synthesized under exclusion of oxygen. With phosphorus pentasulfide the tetrathiafulvalene *S*-oxides **102** can be converted back to the TTF.[207]

The TTF, TSF, and TTeF have several bands in the ultraviolet-visible spectra. The energy of the longest-wavelength band is strongly influenced by substituents. This band can be found in TTF between 400 and 500 nm, in TSF between 490 and 510 nm, and in TTeF at up to 610 nm. Alkyl substituents shift this band in TTF and TSF bathochromically and aryl substituents hypsochromically compared to the unsubstituted compound. Aryl substituted TTF have a higher extinction coefficient (factor 20) than alkyl substituted TTF. Whereas with increasing magnitude of the ring in cycloalkyl substituted TTF the longest-wave visible absorption is clearly shifted bathochromically, it is only slightly influenced by *p*-substituents in the aryl group.[180] This band is shifted to higher energy when the TTF and TSF are benzo-annelated. By changing the TTF to the corresponding TSF and TTeF one can find a bathochromic shift of the longest-wavelength band. This is consistent with its assignment as a $\pi \rightarrow \pi^*$ transition.[71,209–211] From a comparison of quantum-chemical calculations with experimental absorption spectra an assignment as an $n \rightarrow \pi^*$ transition[211] and a $\pi \rightarrow \sigma^*$ transition[177] is also possible.

As a rule the monocations and dications of TTF and TSF have a long-wavelength band at much lower energy than the corresponding TTF and TSF. Of extreme magnitude is the bathochromic shift in aryl substituted compounds which have donor substituents in the aryl group. Only the dications of the unsubstituted and of the aryl substituted TTF have a absorption at shorter wavelength than the corresponding TTF. In the series of the tetrathiafulvalene monocations and dications the longest-wavelength band is shifted bathochromically by alkyl as well as by aryl substituents as compared to the unsubstituted compound. This band obeys a Hammett correlation in the case of aryl substituted tetrathiafulvalene dications (Figure 2).[180]

^{77}Se NMR spectroscopy shows the formation of a mixture of cis/trans isomers in the synthesis of unsymmetrically substituted TSF. The proton noise-decoupled ^{77}Se NMR spectra of this mixture display four well-resolved lines corresponding to separate signals for cis and trans isomeric compounds. These signals allow the cis/trans isomer ratio to be determined. The coupling constants between the selenium atoms in both rings are different in the cis and the trans structure and allow their assignment to the *cis*- and *trans*-isomer.[212,213]

The mass spectrometric fragmentation of TTF, DSDTF, and TSF shows great similarities within the selenium and within the sulfur series. The main difference between the selenium and the sulfur compounds results from the more facile loss of selenium compared with sulfur, and from the first fragmentation of the molecular ion. Whereas the TSF first lose an alkyne molecule, the TTF first lose an ($S\dot{C}R$) radical.[214]

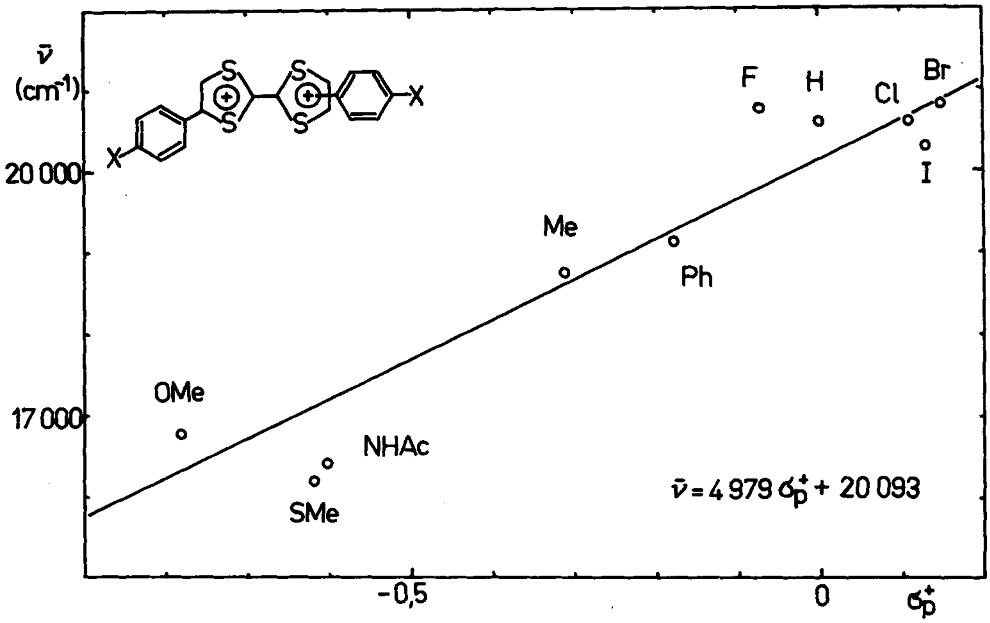


FIGURE 2. Wavenumbers of the longest-wavelength band of 2,6(7)-diaryl substituted TTF dications as a function of substituent constants.

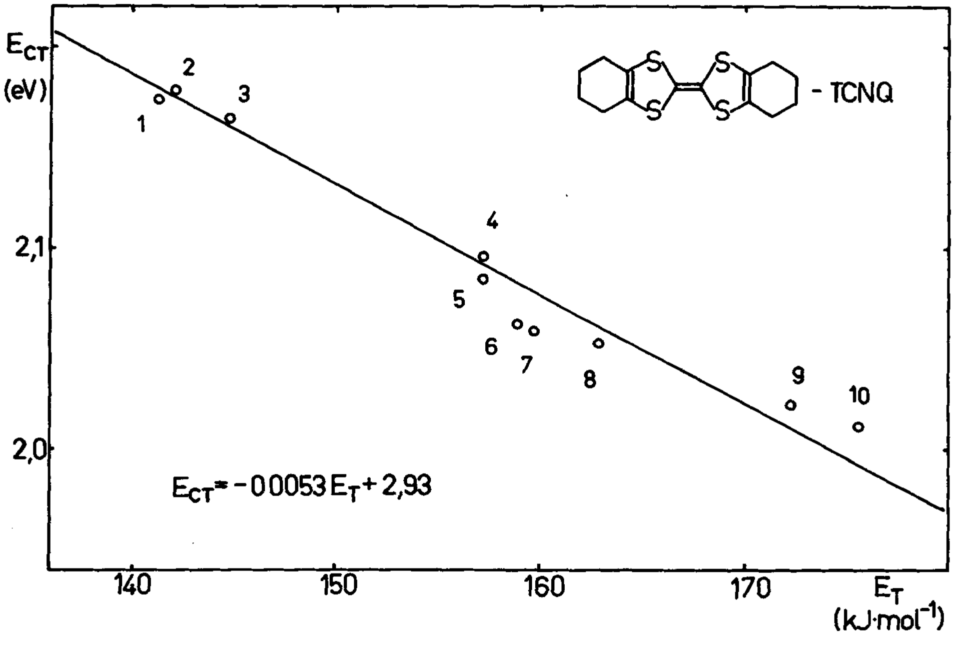


FIGURE 3. Solvent dependence of the charge-transfer absorption of the octamethylenetetrathiafulvalene-TCNQ charge-transfer complex (1 *t*-butylbenzene, 2 toluene, 3 benzene, 4 chlorobenzene, 5 bromobenzene, 6 iodobenzene, 7 1,2-dichlorobenzene, 8 chloroform, 9 dichloromethane, 10 1,2-dichloroethane).

6.3. *Charge-Transfer Complexing of Tetrathia-, Tetraselena- and Tetratellurafulvalenes*

In unpolar solvents TTF form with electron acceptors, like *e.g.* quinones,[215] carbon tetrachloride[178,204] or TCNQ,[216] charge-transfer complexes. In their spectra they show a new absorption which cannot be associated neither with the neutral donor or acceptor nor with their radical cations or radical anions. The energy of this charge-transfer absorption of TTF and TCNQ increases linearly with decreasing E_T values of the solvents (Figure 3) and decreasing oxidation potential of the TTF (Figure 4).[216]

TTF, TSF, and TTeF form with many electron acceptors crystalline charge-transfer salts which possess remarkable electric properties. It was discovered in 1973 that single

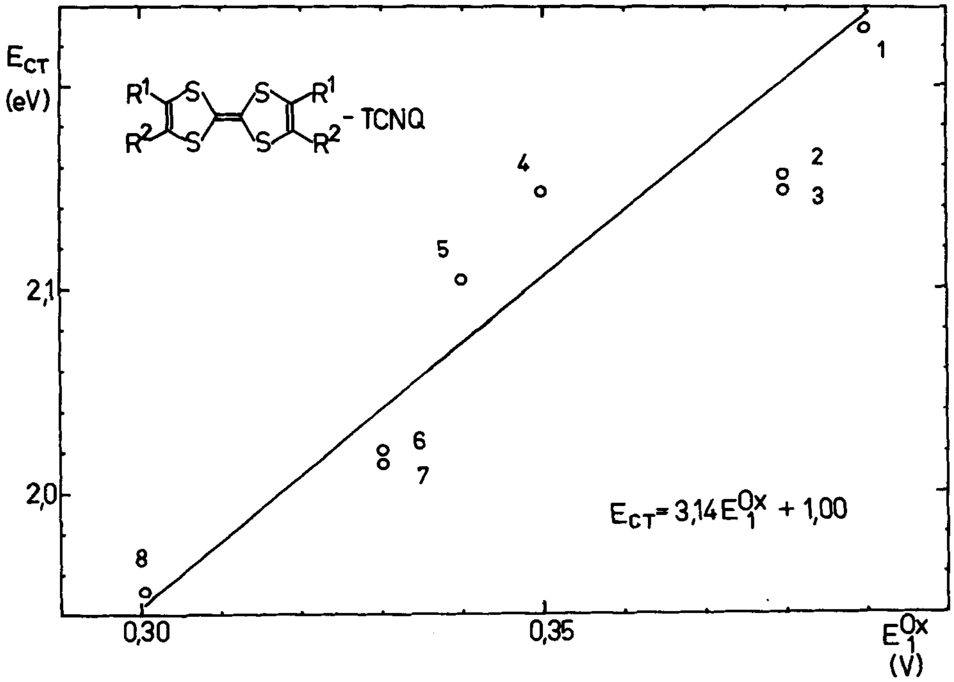


FIGURE 4. Charge-transfer absorption of substituted TTF-TCNQ charge-transfer complexes in chloroform as a function of half-wave oxidation potentials.

	R^1	R^2
1	C_6H_5	H
2	p-ClC_6H_4	H
3	p-BrC_6H_4	H
4	p-$CH_3C_6H_4$	H
5	C_6H_5	CH_3
6	p-$CH_3C_6H_4$	CH_3
7	p-$CH_3OC_6H_4$	H
8	p-$CH_3OC_6H_4$	CH_3

crystals of the charge-transfer complex tetrathiafulvalene-TCNQ show metallic conductivity.[217] Over the years many charge-transfer salts with high conductivity have been encountered.

In the series of TTF, TSF, and TTeF high conductivity of charge-transfer salts is only observed when the following two conditions are fulfilled (in a simplified fashion):

—the donor and the acceptor or only the donor crystallize in segregated and uniform stacks

—partial charge transfer from donor to acceptor in the range from 0.5 to 0.9 electron per molecule takes place

Within the stack the interplanar separations between molecules along the stacking axis are uniform and in the range of the van der Waals radii. Thereby along the stack an overlap of π-orbitals on neighboring molecules arises and a conducting band is formed. By reason of partial charge transfer from donor to acceptor the conduction band is partially filled resulting in a high electron mobility along the stacking axis. Accordingly, the conductivity is much higher in single crystals along the stack than perpendicular to it. An anisotropy of conductivity is the consequence of this system, which is characterized as a one-dimensional conductor. The ratio of the conductivity along the stacking axis to the one perpendicular to it reaches values from 10^2 to 10^3.[218]

In general the charge-transfer salts of TSF exhibit a higher conductivity than the corresponding salts of TTF. Despite diminished donor ability of the TSF in comparison to the TTF the larger orbitals of selenium cause a better overlap of the π-orbitals within the donor stack and allow a better electron transport. Therefore a further enhancement of the conductivity should be expected in the salts of TTeF. The conductivity values obtained by different laboratories for the same complexes are quite different, so that only further investigations of complex composition and crystal structure will give a more exact explanation.[219] Cooling of a single crystal of a one-dimensional conductor causes an increase in the conductivity, which decreases dramatically with further decreasing temperature. This metal-insulator transition can essentially have three reasons.[220]

—For energetic reasons there is a variation of distances between molecules within the stacks. These are no longer uniform and in the simplest cases the molecules dimerize. Thereby the band structure with uncompletely filled bands is lost. Dimerization gives rise to a band splitting with completely filled bands and empty ones and consequently an insulating state (Peierls transition).

—The Coulomb repulsion between electrons within a molecule stack is more important than any possible interaction with the lattice. In this way the electron mobility is decreased as a result of a spin orientation in alternating fashion. One observes an insulating magnetic state, called a spin density wave (SDW) state.

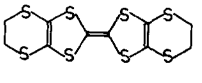
—In some charge-transfer salts with inorganic anions (*e.g.* $BF_4^{\ominus}$, $ClO_4^{\ominus}$, $ReO_4^{\ominus}$, $PF_6^{\ominus}$, $SbCl_6^{\ominus}$, $AsF_6^{\ominus}$) there is an ordered array of these anions with a periodicity of 2a (a = lattice constant). This causes in most cases a gap in the band structure and thus semiconducting behavior.

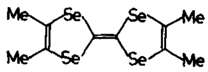
The charge-transfer salts are three-dimensional crystals and therefore there is not only an intrastack electronic interaction, but also interstack electronic coupling. With increasing two- or three-dimensional character of electronic interactions the metal-insulator transition appears not so pronounced or is suppressed.

Application of pressure on charge-transfer salts squeezes the molecules closer together intrastack as well as interstack. On the one hand the conductivity increases thereby and on the other hand the metal-insulator transistion is partially or completely suppressed.

The formation of segregated and uniform stacks with partial charge-transfer from donor to acceptor essentially depends on steric and electronic properties of both complexing agents and crystallization conditions. The investigation of these problems is subject to many conferences and reviews, some which are referred to here.[1-16]

So far the synthetic efforts have been most successful in the cases of the tetramethyltetraselenafulvalenium salt $(TMTSF)_2ClO_4^{17}$ and of the bis(ethylenedithio)tetrathiafulvalenium salts $(BEDT\text{-}TTF)_2I_3$[69,221-223] and $(BEDT\text{-}TTF)_2AuI_2$,,[9,18] which exhibit down to 1.3 K, 2.5 K, and 5 K, respectively, metallic conductivity, followed by transition into the superconducting state.


BEDT-TTF


TMTSF

Some further examples of charge-transfer complexes with high conductivity and semiconducting properties are shown in Table 3.

TABLE 3

Electric conductivity, temperature of metal-insulator transition and structure of selected charge-transfer complexes

Complex	$\sigma_{RT}(\Omega^{-1}\cdot cm^{-1})$	T_{MI}(K)	Structure	Reference
TTF-TCNQ	600	53, 38	D, A	224–226
DSDTF-TCNQ	550	45	D, A	71, 227
TSF-TCNQ	800	28	D, A	119, 227, 228
TMTTF-TCNQ	600	34	D, A	229, 230
TMTSF-TCNQ	1000	57	D, A	231, 232
HMTTF-TCNQ	500	50, 43	D, A	233
HMTSF-TCNQ	1800	no	D, A	234, 235
HMTTeF-TCNQ	550		D, A	219
OMTTF-TCNQ	10^{-5}	–	DA	46, 236
TTF-TNAP	40	185	D, A	237
HMTSF-TNAP	2400		D, A	238, 239
TMTTF-TCNTP	0.2^a			240, 241
DBTTF-TCNQ	10^{-7}	–	DA	47, 61, 242
DBTTF-2,5-TCNQF$_2$	10^{-6}	–	DA	242
DBTTF-2,5-TCNQCl$_2$	40	180	D, A	243, 244
DBTSF-TCNQ	$2.3\cdot10^{-6}$	–	DA	139
DBTSF-2,5-TCNQCl$_2$	20		D, A	139
TTF-chloranil	$8\cdot10^{-4}$	–	DA	245, 246
TTF-Br	10^{-6}	–	DD	193
TTF-Br$_{0.76}$	500	180	D	193, 247, 248
$(TMTTF)_2ClO_4$	30	70	D	249–251
$(TMTSF)_2ClO_4$	500	no	D	17, 252, 253
$(BEDT\text{-}TTF)_2ReO_4$	200	81	D	254, 255
$(BEDT\text{-}TTF)_2I_3$	250	no	D	221, 223, 256
$(BEDT\text{-}TTF)_2AuI_2$		no	D	18

a) compressed pellet

D donor stack, A acceptor stack, DA mixed stack, DD donor dimers, DSDTF diselenadithiafulvalene, TTF tetrathiafulvalene, TSF tetraselenafulvalene, TMTTF tetramethyltetrathiafulvalene, HMTTF and HMTSF and HMTTeF resp. hexamethylenetetrathiafulvalene, -tetraselenafulvalene, and -tetratellurafulvalene, resp., OMTTF octamethylenetetrathiafulvalene, DBTTF and DBTSF, resp., dibenzotetrathiafulvalene and -tetraselenafulvalene, resp., TNAP 11,11,12,12-tetracyano-2,6-naphthoquinodimethane, TCNTP 13,13,14,14-tetracyano-4,5,9,10-tetrahydro-2,7-pyrenoquinodimethane, 2,5-TCNQF$_2$ and TCNQCl$_2$, resp., 2,5-difluoro- and 2,5-dichlorotetracyanoquinodimethane

Doping of an electrically insulating polymer (polyesters, polycarbonates, polysulfones, polyacrylates, polyacetals) with such a highly conducting charge-transfer complex provides an electrically conductive polymer. The conductivity increases by more than 15 orders of magnitude at a doping level lower than 1 wt.%. It can be explained by the fact that the conductive charge-transfer complex is not statistically dispersed in the polymer matrix of the system considered, but forms dendrite-like structures. These electrically conductive compositions can be used as antistatic and conductive layers in electrographic, electrophotographic, and photographic elements.[257–260]

UV illumination of a TTF-halocarbon charge-transfer complex on a surface (glass, paper) forms a coloured TTF radical salt with conductive properties. After subsequent electrolytic deposition of metal from a metal salt solution the conductive pattern can be used as a printed circuit. During the metal deposition the organic layer is simultaneously removed which results in a high adhesion of the metal image to the surface.[204,205,261]

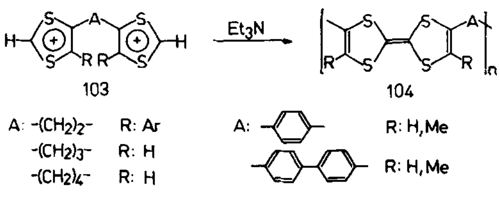
Conducting charge-transfer salts with TTF as donors and halogens as acceptors can be used as electron beam resist materials. Exposure of the charge-transfer salt to an electron beam causes the reverse of the charge-transfer forming TTF and halogen. The reaction products can be sublimed (positive resist) or the unexposed areas dissolved in polar solvents (negative resist). The unexposed parts of the resist are conducting and therefore no build-up of charge occurs and no loss of resolution is caused.[262]

7. SYNTHESIS AND PROPERTIES OF POLYMERIC TETRATHIAFULVALENES

The high electric conductivity of tetrathiafulvalene charge-transfer complexes has also stimulated the synthesis of polymers with tetrathiafulvalene units. Thus many polymers with tetrathiafulvalene units have been prepared by different synthetic methods.

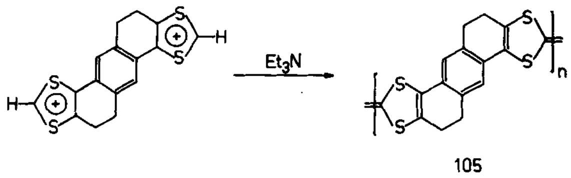
7.1 Deprotonation of Bis-1,3-dithiolium Salts

In a manner analogous to the synthesis of 1,3-dithiolium salts (see Sect. 1.2.) the bis-1,3-dithiolium salts **103** can be synthesized and converted with tertiary aliphatic amines (*e.g.* triethylamine) in acetonitrile to the polymeric TTF **104**.[263–266]



Terminal group analysis showed that the molecular weight (M_n) of the prepared polymeric TTF **104** was about 2000–4000. The polymers **104** are insoluble in all common solvents. Only in sulfuric acid are they soluble by virtue of oxidation to the dications of the TTF unit. With lead(IV) oxide in acetonitrile oxidation to the dication occurs, too. The weaker oxidants bromine and iodine oxidize the polymeric TTF **104** only to the monocations of the TTF unit which can be characterized ESR spectroscopically via a structureless singlet.[264-266] Iodine or TCNQ converts the polymeric TTF **104** to the corresponding charge-transfer complexes with semiconductor properties. Arylene-bridged polymeric tetrathiafulvalene radical salts with their conjugation along the chain possess a higher conductivity, by several orders of magnitude, than the alkylene-bridged derivatives.[266]

Deprotonation of the corresponding bis-1,3-dithiolium salt provides the planar polytetrathiafulvalene **105**. Doping with iodine increases the conductivity of the polymer **105** to $10^{-3}\ \Omega^{-1}\cdot\text{cm}^{-1}$.[267]

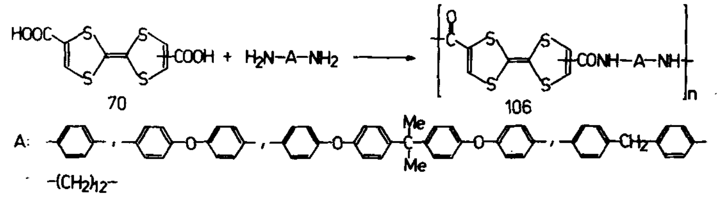


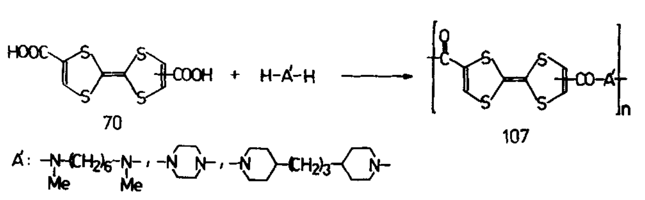
Polymeric TTF **104** can be used as a catalyst in electrodes for fuel cells. Addition of tetrathiafulvalene polymer to a carbon electrode decreases the activation energy for the cathodic oxygen reduction.[268]

Also polymeric TTF **104** are suitable for ion sensitive electrodes as membrane active substances. Especially, they surpass hitherto known electrodes as an iodide sensitive electrode over a wide range of concentrations with short potential adjusting time and low sensitivity for chloride and bromide.[269]

7.2. Polycondensation of Tetrathiafulvalene Derivatives

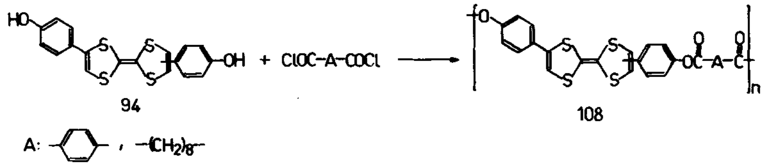
Bivalent tetrathiafulvalene derivatives condense with bivalent amines, alcohols, carboxylic acids, isocyanates, or sulfonyl chlorides to form polyamides,[270,271] polyesters,[272,273] polyurethanes,[274,275] and polysulfonates[275] respectively.



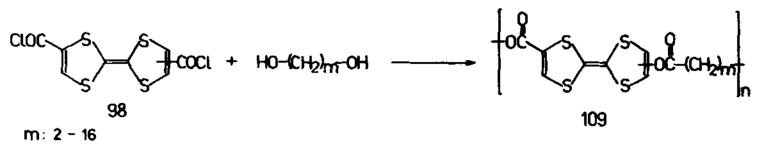


The polycondensation of the diacid **70** with amines was readily effected in *N*,*N*-dimethylformamide at 70 °C with diphenyl phosphite/pyridine[270] or in hexachloroethane with triphenylphosphine/pyridine[271] as dehydratation reagent. The polyamides **106** and

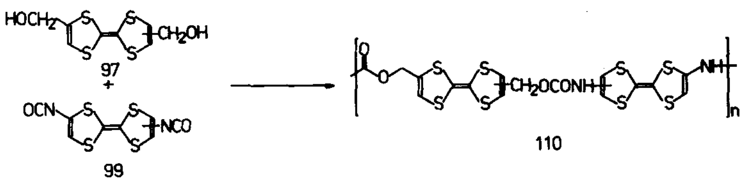
107 are only soluble in trifluoroacetic acid, hexamethylphosphoramide, or dimethyl sulfoxide. With TCNQ they do not form a charge-transfer complex.[270] With bromine the tetrathiafulvalene unit is oxidized to the monocation, causing an increase in the conductivity ($\sigma_{RT} \leqslant 10^{-5}\ \Omega^{-1}\cdot cm^{-1}$).[271]



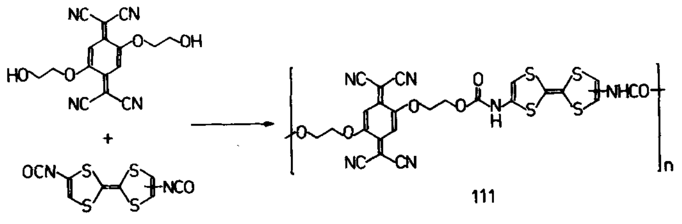
The polyesters **108** are completely soluble in trifluoroacetic acid and soluble in *N,N*-dimethylformamide, dimethyl sulfoxide, and hexamethylphosphoramide. They do not form any charge-transfer complexes with TCNQ, but can be oxidized with bromine to radical salts.[272]



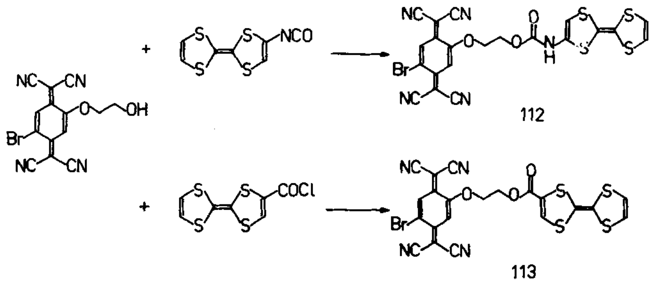
The polyesters **109** (n:3–5; M_n 2000) are insoluble in organic solvents. Upon grinding of the polyesters **109** with TCNQ their conductivity is enhanced by one to five orders of magnitude ($\sigma_{RT} \leqslant 10^{-7}\Omega^{-1}\cdot cm^{-1}$).[273]



The brown polyurethane **110** is insoluble, but can be oxidized with iodine, whereby the conductivity is increased by two orders of magnitude ($\sigma_{RT} = 2\cdot 10^{-6}\Omega^{-1}\cdot cm^{-1}$).[172]



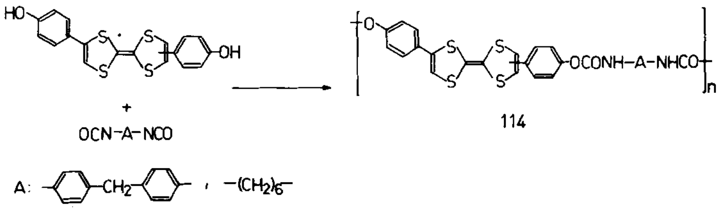
In the same manner a charge-transfer polymer **111** containing covalently bound TCNQ has been prepared. The black polyurethane **111** is amorphous and possesses an electric conductivity of $1.7\cdot 10^{-7}\Omega^{-1}\cdot cm^{-1}$.[172]



112

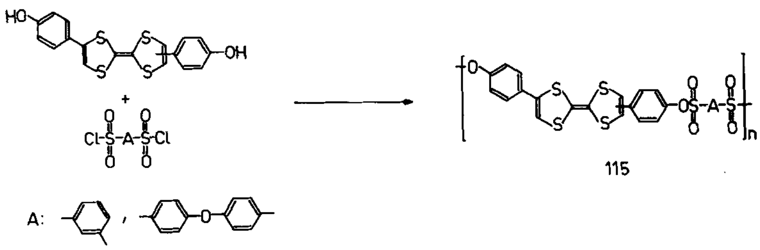
113

The monomers **112** and **113** of similar structure have also been synthesized. Both appear to be zwitterionic.[173]



114

The polyurethanes **114** as well as the polysulfonates **115** are readily soluble in trifluoroacetic acid at room temperature and in *N*,*N*-dimethylformamide, dimethyl sulfoxide,



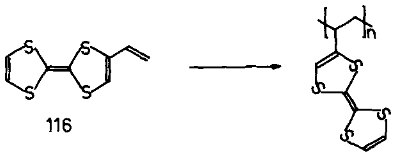
115

and hexamethylphosphoramide upon heating. They form no charge transfer complexes with TCNQ, but can be oxidized with bromine.[274]

7.3. Polymerization of Tetrathiafulvalene Vinyl Monomers

Tetrathiafulvalene vinyl monomers can be polymerized under various reaction conditions.

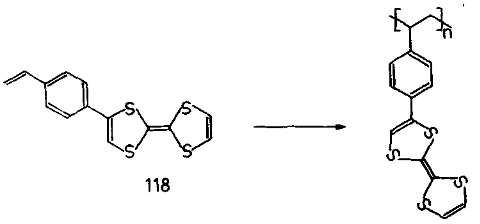
The vinyltetrathiafulvalene **116** can be polymerized thermally as well as by u.v. initiation, azobisisobutyronitrile, or by adding TCNQ, and forms low-molecular weight



116

117

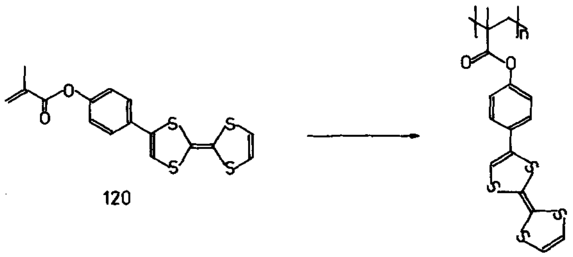
polymers **117**. This polymer **117** forms with bromine or TCNQ charge-transfer complexes.[174]



118

119

The polymerization of (*p*-vinylphenyl)tetrathiafulvalene **118** was carried out in a sealed tube *in vacuo* at 130 °C for 3 days. A polymer **119** with a molecular weight of about 50,000 was isolated. The brown polymer **119** is insoluble in all usual organic solvents. With bromine the polymer **119** is oxidized and its conductivity increases by two orders of magnitude to $10^{-8}\,\Omega^{-1}\cdot\text{cm}^{-1}$. The anionic polymerization or initiation with azobisisobutyronitrile was unsuccessful.[276]



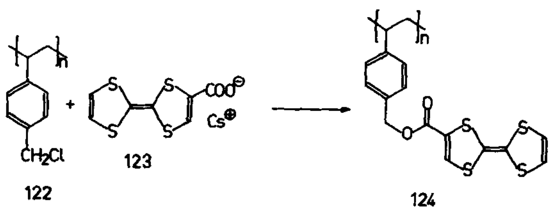
120

121

The polymerization of *p*-(2-tetrathiafulvalenyl)phenyl methacrylate **120** is only successful in a sealed tube *in vacuo* upon heating at 120 °C for 48 hours. The black polymer **121** is only soluble in strong acids. It is converted with bromine to a bromine complex. The copolymerization with methyl methacrylate gives a soluble copolymer with a molecular weight (M_n) of about 10,000 (93.5% of MMA).[169]

7.4. Reactions of Polymers

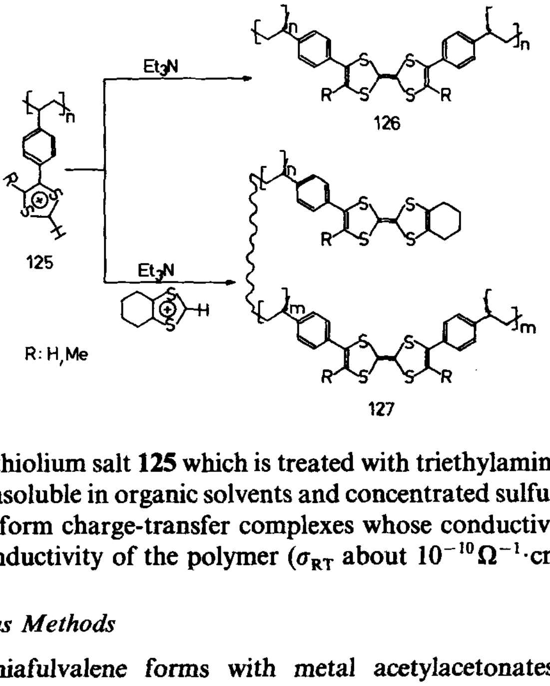
Another polymeric tetrathiafulvalene is formed by reaction of a linear poly(vinylbenzyl chloride) **122** with the cesium salt of carboxytetrathiafulvalene **123**, where 30% of the sites have reacted with the tetrathiafulvalene moiety.



The tetrathiafulvalene substituted polystyrene **124** is soluble in tetrahydrofuran and films can be prepared.[275]

Such a polystyrene derivative with attached tetrathiafulvalene units is used as negatively working photoresist. Illumination of the polymer in the presence of carbon tetrabromide converts the weakly polar polymer to a more polar polymer, which is insoluble in solvents of low polarity (ether, ketones). After treatment with solvents the insoluble areas do not swell and therefore the resolving power is increased.[277]

Tetrathiafulvalene substituted polystyrenes **126** and **127** are also obtained by acylation of an atactic polystyrene (M_n 3200) with α-haloacid halides and further conversion

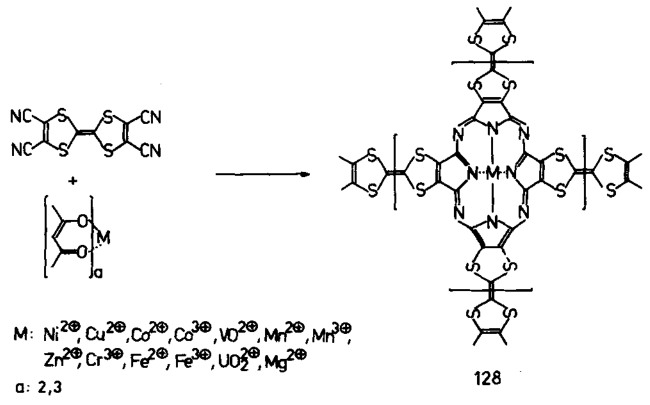


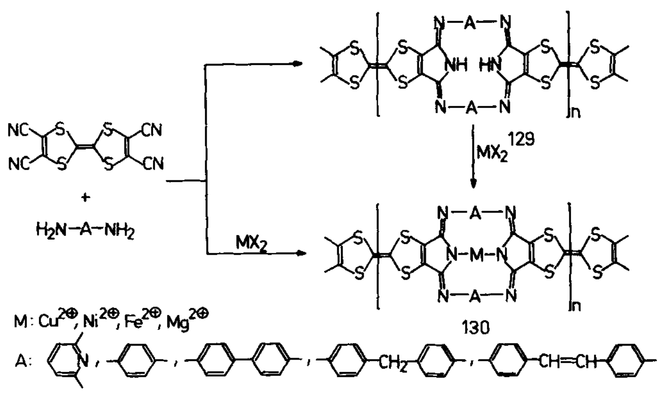
corresponding dithiolium salt **125** which is treated with triethylamine.[278] These polymers **126** and **127** are insoluble in organic solvents and concentrated sulfuric acid. With iodine and TCNQ they form charge-transfer complexes whose conductivity differs only little from that the conductivity of the polymer (σ_{RT} about $10^{-10}\Omega^{-1}\cdot cm^{-1}$).[278]

7.5. Miscellaneous Methods

Tetracyanotetrathiafulvalene forms with metal acetylacetonates polymers with a phthalocyanine-like structure **128** and with diamines polymers of the hemiporphyrazine type **129**, both containing tetrathiafulvalene units.[279,280]

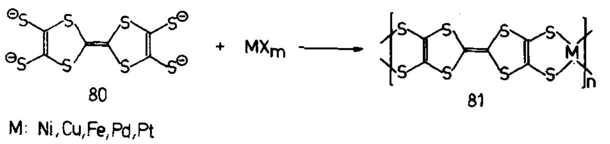
Both types of polymers **128** and **129** are dark coloured, insoluble in all solvents and show semiconductor properties ($\sigma_{RT} < 10^{-5}\Omega^{-1}\cdot cm^{-1}$). In the case of the hemiporphyrazine type polymers **129** the two hydrogen atoms inside the macroheterocyclic ring can be substituted by metal atoms. Depending on the metal atom and the bridging group A the electric conductivity increases up to two orders of magnitude.[280]





7.6. Polymeric Tetrathiafulvalene Metal Bisdithiolene Complexes

The reaction of tetrathiafulvalenetetrathiolate **80** with metal salts leads to the precipitation of insoluble, amorphous powders **81** with high electric conductivity (M: Cu $\sigma_{RT} = 10^{-1}\,\Omega^{-1}\cdot\text{cm}^{-1}$).[44,162,164]

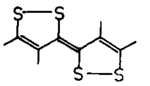


A ribbon, but also two-dimensional layers could be formed. Qualitative MO and band structure calculations support this assumption.[281]

8. SYNTHESIS OF 1,2-TETRATHIAFULVALENES (1,2-TTF)

While the 1,3-tetrathiafulvalenes (TTF) have been known for many years, especially since the discovery of the high electric conductivity of their charge-transfer complexes, and a lot of new and efficient syntheses have been described, the chemistry of the analogous 1,2-tetrathiafulvalenes (1,2-TTF) **131** is poorly developed. The first synthesis of 1,2-TTF was reported in 1975.[282]

Most pathways to 1,2-TTF start from the 1,2-dithioles **132–136**. In this paper we are only reviewing some of the common possibilities for the synthesis of these compounds (for more detailed information see reviews[51,52,283–285]).



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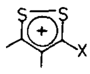


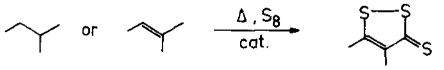
132 136

	132	133	134	135	136
X	$S^{\ominus}$	$O^{\ominus}$	H	Cl	SR

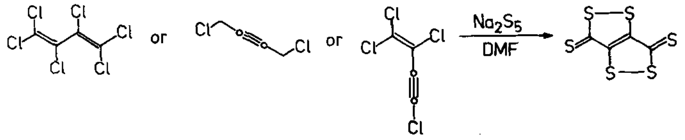
8.1. *Synthesis of 1,2-Dithiole Derivatives*

8.1.1. 1,2-Dithiole-3-thiones 1,2-Dithiole-3-thiones (trithiones) **132** are available by high-temperature sulfurization (200–500 °C) of the hydrocarbons **137** or **138** and their derivatives.[286] The yields are good in some cases and can be increased by the use of basic catalysts (*e.g.* diphenylguanidine).[287]

Polyhalogenated hydrocarbons can be thiated at lower temperatures in aprotic solvents (*e.g.* **139**,**140**, **141** to **142**).[288]

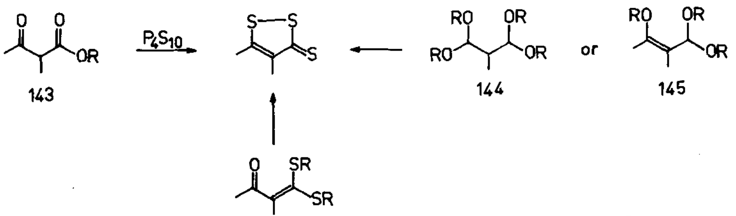


137 138 132

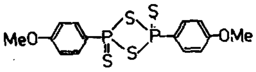


139 140 141 142

A very efficient way to the trithiones **132** is the sulfurization of *β*-keto esters **143** and their functional derivatives (*e.g.* **144–146**) with phosphorus pentasulfide,[289,290] preferably in the presence of sulfur.[291] In many cases the yields can be remarkably increased by using the 2,4-diphospha-1,3-dithietane **147** (Lawesson's reagent) as sulfurization agent.[292]

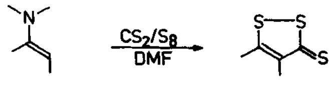


143 144 145 146



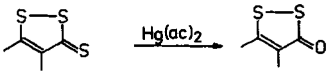
147

Another common way to trithiones **132** starts from enamines **148**, carbon disulfide, and sulfur.[293]



148 132

8.1.2. 1,2-Dithiol-3-ones The 1,2-dithiol-3-ones **133** can be obtained from the corresponding 1,2-dithiole-3-thiones by desulfurization with mercuric acetate.[72]

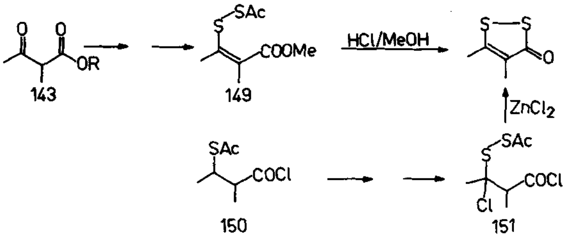


132 133

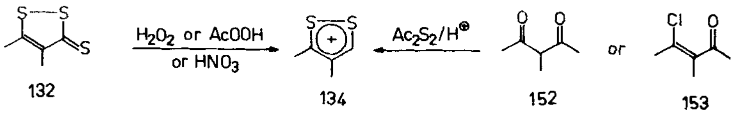
Furthermore, 1,2-dithiol-3-ones **133** can be synthesized from acyclic compounds. For instance the sulfurization of cinnamic esters with sulfur at 250 °C gives 5-phenyl-1,2-dithiol-3-one in yields up to 65%.[294]

A common method used to otbain 1,2-dithiol-3-ones **133** starts from β-keto esters **143** and leads to the 1,2-dithiol-3-ones via the β-acetyldithioacrylic esters **149**.[295]

In a similar way the β-acetyl thioacid chlorides **150** give the compounds **133** via the β-acetyldithio-β-chloro acid chlorides **151**.[296]

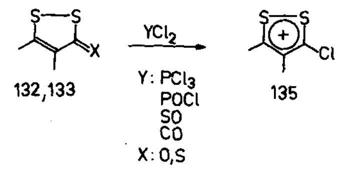


8.1.3. 3H-1,2-Dithiolium salts 3*H*-1,2-Dithiolium salts **134** can be obtained in a manner similar to that for 2*H*-1,3-dithiolium salts **16** by oxidation of the corresponding trithiones with peracetic acid,[297] hydrogen peroxide,[298] or nitric acid.[299] Furthermore they are available from acyclic educts (*e.g.* **152** or **153**) by reaction with diacetyl disulfide in the presence of strong acids.[300]

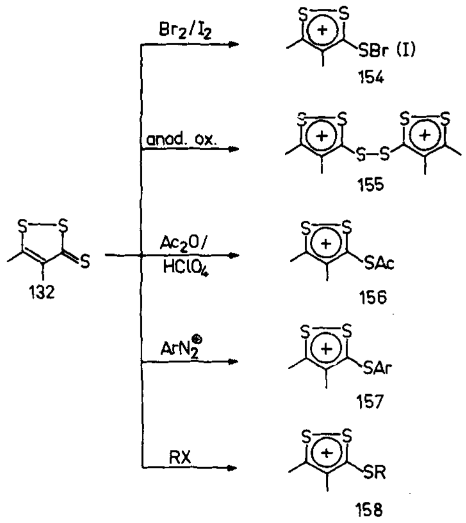


132 134 152 153

8.1.4. 3-Chloro-1,2-dithiolium salts 3-Chloro-1,2-dithiolium salts **135** can be synthesized from the corresponding 1,2-dithiole-3-thiones **132** or 1,2-dithiol-3-ones **133** by reaction with halogen transfer compounds (*e.g.* phosphorus pentachloride,[301] oxalyl chloride,[301,302] phosphorus oxychloride[301]).



8.1.5. Organylthio-1,2-dithiolium salts 1,2-Dithiole-3-thiones **132** are compounds with a strongly polar thione group which can easily be attacked by electrophiles. With halogens the sulfenyl halides **154**[303] and by anodic oxidation the disulfides **155**[304] are formed. In the presence of perchloric acid the acylation to the reactive acylthiodithiolium salts **156** is possible.[305] Diazonium salts arylate to the 3-arylthio-1,2-dithiolium salts **157**.[306] Due to the simple replacement of the arylthio group by nucleophiles and due to their simple availability[307] especially the 3-alkylthio-1,2-dithiolium salts **158** are of high preparative interest.



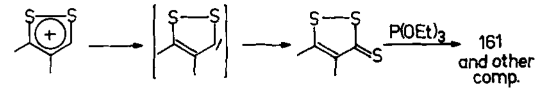
8.2. Unsuccessful Attempts to Synthesize 1,2-TTF

All attempts to make 1,2-TTF by deprotonation of the 3*H*-1,2-dithiolium salts **134** via the corresponding carbenes **159** failed. The deprotonation of the 3*H*-1,2-dithiolium salts **134** leads to product mixtures from which 1,2-dithiole-3-thiones **132**,[308,309] thiathiophthenes **160**,[310] thieno[3,2-*b*]thiophenes **161**[311] and a thieno[3,2-*c*]dithiin **162**[309] could be isolated. The formation of these compounds can be explained via the 3-carbena-1,2-dithiole **159** as intermediate. Other reasons for the postulation of the carbene **159** as the primary deprotonation product of the dithiolium salts **134** are the results of the base catalyzed H/D exchange[308,312] and the observation that the yields of trithiones **132** increase remarkably if the deprotonation is carried out with additional amounts of sulfur.[308]

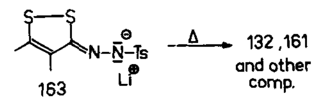
Also, thermolysis of alkali salts of 1,2-dithiol-3-one hydrazones **163** leads not to 1,2-TTF, but to compounds of the type **132** and **161**.[309]

Furthermore, the reaction of trithiones **132** with trivalent phosphorus compounds

—very successful in the synthesis of 1,3-TTF—leads to the thieno[3,2-*b*]thiophenes **161**.[309,313] Only alkylthio substituted trithiones **132** form with triethyl phosphite the corresponding 1,2-TTF (Table 12)[313a].



134 159 132



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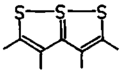

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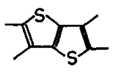

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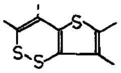
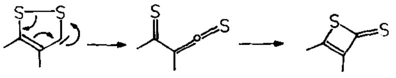


162

An explanation of the experimental observation that the postulated carbene **159** as intermediate yields not 1,2-TTF has been given.[314] The authors made quantum chemical calculations on a CNDO/2 basis. They came to the conclusion that the carbenes **159** isomerize very fast to the thiete-2-thiones **165** with S–S bond cleavage. The open-chain thioacyl thioketenes **164** are discussed as intermediates. According to this calculation the possible dimerization of the carbene **159** to the 1,2-TTF is kinetically depressed by competing reactions.

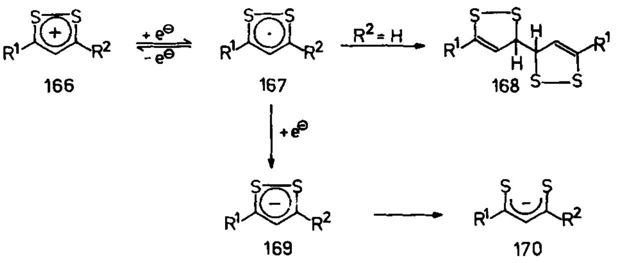


159 164 165

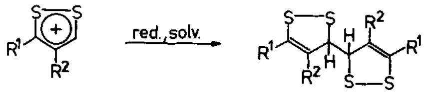
8.3. *Synthesis of 1,2-TTF*

8.3.1. 1,2-TTF by Reductive Dimerization of 1,2-Dithiolium salts The cathodic reduction of the dithiolium salts **166** leads, with reception of one electron, to the corresponding 1,2-dithiolium radical **167**, which can dimerize to compound **168**.[315] The stability of the radical **167** and the equilibrium **167** ⇌ **168** depend on the nature of the substituents R^1 and R^2 and the temperature. Whereas in the case of the radicals **167** with $R^2 = H$ the equilibrium lies definitely on the side of the dimers the equilibrium in the case of **167** with $R^1 = R^2 = Ph$ lies on the opposite side. Reception of a further electron leads to the dithiolium anions **169**. This reduction step is irreversible, the reason being the formation of the dithiodiketonate anion **170**. The intermediate steps **166**–**170** can also be carried out photochemically.[315]

Preferred reagents for preparative reductions for the synthesis of the dimers **171** are zinc and aqueous titanium(III) chloride solutions.[316]

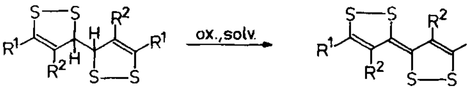


Preferred reagents for preparative reductions for the synthesis of the dimers **171** are zinc and aqueous titanium(III) chloride solutions.[316]



134 171

Contrary to earlier claims[317] some dimers **171** could be dehydrogenated by several oxidation agents to the 1,2-TTF **131**.[282,316] For 1,2-TTF by dehydrogenation of the dimers **171**, see Table 10.



171 131

	a	b	c	d	e	f
R^1	Ph	Ph	Ph	H	H	$-(CH{=}CH)_2-$
R^2	H	Me	Ph	Ph	H	

The oxidation of the dimers **171** with iodine or bromine or their electrochemical oxidation leads to the dithiolium salts **134**.

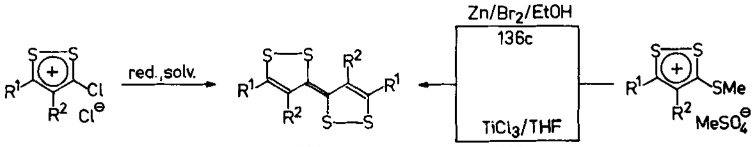
Reduction of 3-chloro-1,2-dithiolium salts **135** with zinc, silver, or aqueous titanium(III) chloride solution gives the 1,2-TTF **131** in one step.[316]

The conversion of the 3-methylthio-1,2-dithiolium salt **136c** to **131c** requires zinc as reducing agent and bromine as oxidative "extractor" for the alkylthio groups.

Reduction of the compound **136a** with titanium(III) chloride alone gave the 1,2-TTF **131a** in only about 3% yield.

1,2-TTF corresponding to the dimers **171d,e** could not be synthesized.

1,2-TTF by reduction of the dithiolium salts **135** and **136**, see Table 11.

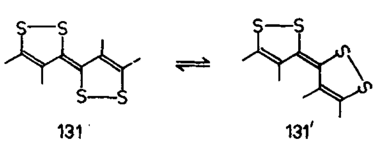


135 131 136

	a	c
R^1	Ph	Ph
R^2	H	Ph

The choice of the reduction agent and the reduction conditions (solvent, temperature) have a great influence on the success of the dimerization reaction.[316]

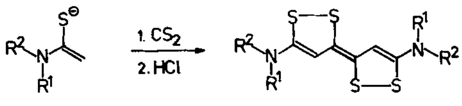
The 1,2-TTF **131a** and **131f** could be isolated in two isomeric forms, characterized by their different u.v.-vis. spectra. The conversion of one form into the other—considered as the *cis-trans* isomers **131/131′**—can be carried out thermally or photochemically. In the cases of the 4-methyl and 4-phenyl substituted compounds **131b** and **131c** only one isomer could be isolated.



131 131′

Besides the 1,2-TTF the reaction mixtures also contain the corresponding trithiones **132**, in some cases additionally 1,2-dithiol-3-ones **133** and thieno[3,2-*b*]thiophenes **161**. The intermediate formation of the carbenes **159** has been discussed as one of the reasons for this observation.

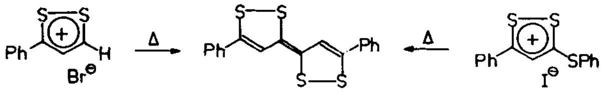
8.3.2. Formation of 1,2-TTF in Other Ways A further approach to 1,2-TTF starts from the thiolates **172**. Reaction of **172** with carbon disulfide, followed by treatment with hydrochloric acid, yields the amino substituted 1,2-TTF **131g–j** in 7–30% yield.[318]



172 131

	R^1	R^2
g	Me	Me
h	$-(CH_2)_5-$	
i	$-(CH_2)_2-O-(CH_2)_2-$	
j	Me	Ph

Already before the first announcement of the preparation of 1,2-TTF[319] the possible formation of 1,2-TTF by thermolysis of the salts **134a** or **136k** in the ion source of a mass spectrometer was reported. This was confirmed in a later publication.[320]



134a 136k

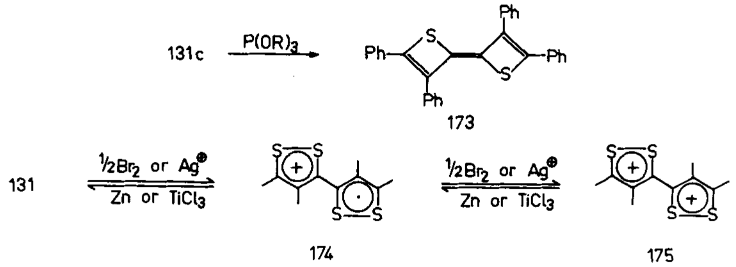
9. PROPERTIES OF 1,2-TETRATHIAFULVALENES

The 1,2-TTF are deep coloured solids, which are only sparingly soluble in most solvents. Of the amino substituted compounds if is only reported that they are yellow. The 1,2-TTF are thermally less stable than the 1,3-TTF. In boiling tetraline compound **131c** is converted to the thieno[3,2-*b*]thiophene **161** in about 80% yield.[282,308]

Other 1,2-TTF react analogously. In some cases addition of sulfur during the thermolysis is a further reaction so that the trithiones **132** and a thienodithiine **162** can be isolated.

The reaction behaviour of 1,2-TTF with trivalent phosphorus compounds was studied in example **131c**. Whereas no reaction took place with triphenylphosphine in boiling benzene, with triethyl phosphite or tributyl phosphite a new compound was formed which contains two sulfur atoms less than **131c**. As a possible structure **173** was postulated.

In their redox properties the 1,2-TTF show great similarity to the 1,3-analogues. Depending on the nature and amount of the oxidizing agent, oxidation to the radical cation **174** or the dication **175** takes place. The neutral 1,2-TTF comproportionate with the dications **175** to the radical cations **174**. Zinc or titanium(III) chloride reduces the salts **174** and **175** to the neutral 1,2-TTF. The 1,2-TTF are typical reversible redox systems.[308]

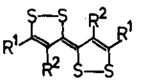


9.1. Charge-Transfer Complexes of 1,2-TTF

Like the analogous TTF the 1,2-TTF also form charge-transfer complexes with several acceptors (Table 4). Only 1:1 donor-acceptor complexes have been isolated. In the electron spectra of the charge-transfer complexes long-wavelength absorptions of the donor and acceptor radical ions have been identified. Although the first isolation of a charge-transfer complex from a 1,2-TTF and TCNQ was reported in 1975[282] the experimental data available until now are very limited. General conclusions about the dependence between structure and redox properties or electric conductivity of the donors **131** and their charge-transfer complexes cannot be drawn.

TABLE 4

Charge-transfer complexes of 1,2-TTF with acceptors and their electric conductivity (compressed powder)

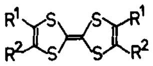


R^1	R^2	acceptor	σ_{RT} ($\Omega^{-1}\cdot cm^{-1}$)	reference
Ph	H	DDQ[a)]		316
		TCNQ[b)]	3–5	321
Ph	Ph	DDQ	10^{-5}	316, 322
		TCNE[b)]		316
		TCNQ	10^{-5}	322
		$TCNQF_4$	10^{-3}	322
Ph	SMe	$TCNQF_4$	10^{-5}	322
SMe	SMe	TCNQ	10^{-5}	322
$-(CH=CH)_2-$		DDQ		316
$-CH=CH-S-$		TCNQ	10^{-3}	322

a) both isomeric forms provide the same complex
b) only one of the isomeric forms provides a complex
DDQ: 2,3-dichloro-5,6-dicyanobenzoquinone, TCNE: tetracyanoethylene, $TCNQF_4$: tetrafluorotetracyanoquinodimethane

TABLE 5

Molecular properties of TTF (redox potential in acetonitrile vs. sce)



Formula 96 R^1	R^2	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
H	H	A	119	91	446 (263), 357 sh, 316 (12,300), 308 (12,200)[a]	0.33 0.1 M TEAP	0.71	34, 55, 58, 175 177, 178
		B Z = S (MeO)$_3$P	(C$_6$H$_{14}$/ c-C$_6$H$_{12}$)	1	450 (230), 368 (2,000), 316 (11,400), 303 (12,800)[b]	0.32 0.1 M TBAP	0.68	22, 82 71
		Z = Se (MeO)$_3$P		70	449 (257), 362 (2,000), 304 (13,100)[c]	0.33 0.05 M TBAT	0.69	71, 180, 323
		I Z = S M = Co$_2$ n = 8		35	450 (270), 368 (1,900), 317 (12,500), 303 (13,300)[d]	0.40 0.05 M TBAT[e]	0.86	99, 177, 323
		M R = Me R = Bu		 33 25		0.31 0.1 M LiCl[f]	0.74	98, 180 98
						0.45 0.1 M TEAT[g]	0.82	58
						0.02 0.1 M TEAP[h]	0.40	324
CH$_3$	H	A	96–100 (EtOH)	30–40	440 (1,340), 355 sh, 321 (13,500), 308 (14,800), 298 (15,800)[b]	0.32 0.1 M TEAP	0.68	22, 82, 175, 325
			109–111[i]		453 (180), 298 (7,500)[c]	0.29 0.1 M TBAP	0.71	22, 325
						0.24 0.05 M TBAT	0.62	323
n-C$_{17}$H$_{35}$	H	A	91–92 (c-C$_6$H$_{12}$)		480 (480), 360 (2,570), 320 (11,700), 300 (12,900)[b]			326
CH$_3$	CH$_3$	A	245 (MeCN)	61	473 (248), 327 (13,800), 315 (14,000), 297 sh, 287 sh[b]	0.24 0.1 M TEAP	0.60	27, 81, 82, 326
		A	240–241 (MeCN)			0.25 0.1 M TBAP	0.62	22, 326
		I Z = S M = Co$_2$ n = 8	244	25		0.21 0.05 M TBAT	0.59	99, 323

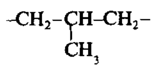
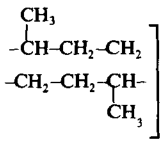
		M R = Bu		77		0.24 TBAA[e]	0.73	97, 141
						0.35 0.2 M TBAT[k]	0.83	142, 327
CD_3	CD_3		241–243 (MeCn)					349
CH_3	C_2H_5	A	102			0.24 0.1 M TBAP	0.61	22
C_2H_5	C_2H_5	A	125			0.23 0.1 M TBAP	0.75	22
n-C_3H_7	n-C_3H_7	A			325 (15,100), 310 (14,200)[a]	−0.06 0.1 M TEAP[h]	0.32	324
n-$C_{16}H_{33}$	n-$C_{17}H_{35}$	A	91–92 (benzene)		480 (400), 330 (12,300), 315 (13,800), 300 (12,300)[b]			326
n-$C_{17}H_{35}$	n-$C_{17}H_{35}$	A	93–95 (benzene)		482 (303)[l]			326
					480, 363, 328, 314, 300[b]			326
$-(CH_2)_3-$		A	244 (MeCN/tri-chlorobenzen)	71	465 (340), 315 (12,300)[m]	0.33 0.1 M TEAP	0.66	28, 46
					462 (177), 327 (9,280), 307 (10,500)[n]	0.31 0.1 M TBAP	0.74	22
		A	254		464 (374), 305 (22,900)[c]	0.26 0.1 M LiCl[f]	0.67	22, 180
		F		50		0.27 0.1 M TEAP	0.60	81, 92
		G	270–274 (benzene)	42				203
		I Z = S M = Co_2 n = 8	243	20				99
 $-CH_2-CH(CH_3)-CH_2-$		A	155–156 (hexane)	32	468 (400), 330 sh, 315 (13,800)[m]	0.30 0.1 M TEAP	0.63	28
 $-CH(CH_3)-CH_2-CH_2$ / $-CH_2-CH_2-CH(CH_3)-$		A	119–120 (EtNO$_2$) 137–139 (hexane)	37	465 (500), 330 sh, 313 (16,600)[m]	0.30 0.1 M TEAP	0.64	28

TABLE 5 (Continued)

R^1	R^2	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
$-(CH_2)_4-$		A	248 (PhCl)	74	472 (195), 323 (9,550), 297 (10,600)[a]	0.40 0.1 M TEAT[a]	0.80	46, 58
		F		74	470 (290), 323 (14,200), 300 (15,100)[a]	0.25 0.1 M LiCl[f]	0.67	58, 92, 180
		G	255–258 (benzene/ MeOH)	57	477 (324), 301 (19,400)[c]			93, 180
		I Z = S M = Co_2 n = 8	245	37				99
		M R = Bu		68				97
$-(CH_2)_5-$		A	199–206 (benzene/ MeOH)	65	500 (236), 291 (23,600)[c]	0.21 0.1 M LiCl[f]	0.64	180, 203
$-CH_2OH$	H		178–180 (EtOH)	13				65
			160					172
$-S-CH_2-CH_2-$		B Z = Se	184–186 ($CHCl_3$)	13	476 (480), 370 sh, 340 sh 323 (20,000), 310 sh[m]	0.43 0.1 M TEAP	0.69	28
$-S-CH_2-CH_2-$ $-CH_2-CH_2-S-$		B Z = Se	195–196 (PhCl)	37	483 (645), 370 sh, 340 sh, 323 (12,600), 310 sh[m]	0.43 0.1 M TEAP	0.69	28
$CH_3SCH_2CH_2$	$CH_3SCH_2CH_2$		110 (MeCN)	60		0.22 0.1 M TEAP[h]	0.47	40
$CH_3COS(CH_2)_3$	$CH_3COS(CH_2)_3$		95	60		0.19 0.1 M TEAP[h]	0.42	40
CH_3	CH_3S		136 (MeCN)	43				105
C_2H_5	CH_3S		86 (MeCN)	69				105
C_6H_5	CH_3S		173 (MeCN)	66				105
p-$CH_3C_6H_4$	CH_3S		190 (MeCN)	38				105

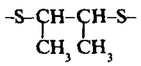
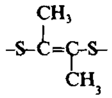
p-ClC$_6$H$_4$	CH$_3$S		186 (MeCN)	76			105
p-ClC$_6$H$_4$	C$_2$H$_5$S		130 (MeCN)	71			105
p-ClC$_6$H$_4$	C$_6$H$_5$CH$_2$S		170 (MeCN)	30			105
CH$_3$S	CH$_3$S	B		56	490 (400), 380 (3,715), 332 (13, 500), 311 (14,450)[t)]	0.49 0.67 0.05 M TEAP	67, 165
		K	94.5–96 (MeCN)	75	370 (1,700), 329 (7,750), 309 (8,700), 260 (7,750)[a)]	0.47 0.71 0.05 M TEAP	39, 81
	–S–CH$_2$–S–	A	154–156		542 (4,080), 354 (4,900), 282 (7,600), 264 (8,100)[k)]	0.57 0.77 0.1 M TBAP[v)]	328, 350
		B Z = O	191–192	48			68, 166
	–S–(CH$_2$)$_2$–S–	B Z = O (EtO)$_3$P	242.5	82	467 (276), 349 (10,960), 324 (14,800)[v)]	0.49 0.74 0.1 M TEAP	68, 81, 166, 329, 330, 351
		Z = S (EtO)$_3$P	> 250	45	490 (400), 347 (10,470), 321 (15, 150)[t)]	0.53 0.77 0.05 M TEAP	67, 165
		Z = S (EtO)$_3$P	258–260 (PhCl)	23		0.55 0.85 0.1 M TBAP[v)]	69, 166, 350
	 $-S-CH(CH_3)-CH(CH_3)-S-$	B Z = S (EtO)$_3$P					352
	–S–(CH$_2$)$_3$–S–	B Z = S (EtO)$_3$P	> 250	45		0.58 0.86 0.05 M TEAP	67
		B Z = O Z = S	265	89 40		0.50 0.78 0.1 M TEAP	81, 166
	–S–CH$_2$–S–CH$_2$–S–	B Z = O (EtO)$_3$P	235–240				68
	–S–CH=CH– –CH=CH–S–	A	214–215 (hexane)	30		0.47 0.74 0.1 M TEAP	28
	–S–CH=CH–S–	B Z = O (EtO)$_3$P	227–230				68
	 $-S-C(CH_3)=C(CH_3)-S-$	B Z = O (EtO)$_3$P	240				68
CH$_3$Se	CH$_3$Se			45			90
C$_6$H$_5$Se	C$_6$H$_5$Se			60			90

TABLE 5 (Continued)

R^1	R^2	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
C_2H_5Te	H		85	20				176
CH_3Te	CH_3Te							176
C_2H_5Te	C_2H_5Te		88–90 ($CHCl_3$)	35				176
$COOCH_3$	H	B Z = S $(EtO)_3P$	244–246 (glyme)	38				65
		D	244–245 (glyme)	21	444 (2,470), 315 (11,000), 302 (10,600), 290 (10,000)[k]			34
		E	242–244 (glyme)	96				88
			226–228	53				159
$COOC_2H_5$	H	D		26				86
		E	169–172 (MeOH)	2				63
			140–160			0.60 0.1 M TEAP	0.94	175
$COOC_6H_4NO_2$-*p*	H	B Z = S $(EtO)_3P$	280 (toluene)	9				65
$COOCOCH_3$	H		~350 (MeCN)	47				65
COOH	H	E	360					88
			>350 (pyridine)		407 (2,570), 313 (13,000), 302 (12,600), 285 sh[c]			34, 65, 66
$CONHC_6H_5$	H		224–226 (MeCN)	72				65
$CON(CH_3)_2$	H		231–232 (CH_2Cl_2/ ether)	22				159
COCl	H		240–245					172
NCO	H		156 (benzene/ heptane)					172

$COOCH_3$	$COOCH_3$	B Z = S $(MeO)_3P$		63	445 (1,930), 315 (13,100), 284 (14,300), 245 (15,500)[p]	0.80 0.1 M TEAP	1.08	63, 66, 204, 331
		Z = S $(EtO)_3P$		52	446[q]			65, 66
		Z = S Ph_3P		90	455[k]			66
		D		28	461[b]			66, 86, 87
		E	169–170 (MeOH)	10	462[l]			63, 66
		E	169–170 (benzene/hexane)	36				91
		E	163–167 (ether/hexane)					88
		I Z = S M = Co_2 n = 8	168	20				99
		M R = Bu		73				97
$CONH_2$	$CONH_2$				449 (2,040), 319 (15,150)[q]			66
COOH	COOH		> 300 (H_2O or acetone)		477 (2,140), 311 (14,800)[q]			65, 66, 91
CF_3	CF_3	B Z = S Ph_3P		89	412 (1,520), 310 (13,600), 222 (12,600)[r]	1.05 0.1 M TBAP	1.28	63
		E	90–91 (sublim.)	100		1.08 0.1 M TEAP		63, 204
CN	CN	B Z = O $(MeO)_3P$	265–267 (CH_2Cl_2)	95	502 (2,000), 328 (15,100)[l]	1.12 0.1 M TEAP	1.22	66, 204, 332, 333
		Z = S $(MeO)_3P$		10–30	500 (2,300), 325 (15,800), 262 (25,700)[m]			64, 66, 332
		Z = S Ph_3P		5	492 (2,000), 323 (14,500), 261 (21,400)[a]			64, 66, 332
		Z = S $(PhO)_3P$		75	480 (2,450), 320 (11,000), 261 (15,800)[s]			66, 332
		I Z = S M = Fe_3 n = 12		10				64
CHO	CHO	I Z = S M = Co_2 n = 8	280	60				36

TABLE 5 (Continued)

R^1	R^2	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
Br	H					0.59 0.1 M TEAP		204
C_6H_5	H	A	202–206 (benzene)	30–40	403 (2,700), 329 (9,000), 259 (12,100)$^{c)}$			325
		F		73	416 (5,950), 331 (22,900) 258 (36,640)$^{c)}$	0.39 0.1 M LiCl$^{f)}$	0.78	92, 180
		G	207–213 (benzene/ MeOH)	64				203
		I Z = S M = Co_2 n = 8		25				99
		M		5				96
p-HOC_6H_4	H		207–208 (MeOH)					65
m-HOC_6H_4	H		224–225 (MeOH)					65
p-$CH_3OC_6H_4$	H	A	254–256 (benzene/ ether)	30–40	392 (5,100), 332 (12,100), 270 (22,700)$^{c)}$			325
		G	256–261 (benzene/ MeOH)		404 (6,080), 334 (18,090), 271 (38,500)$^{c)}$	0.33 0.1 M LiCl$^{f)}$	0.73	180
p-$CH_3SC_6H_4$	H	A	249–253 (DMF)	88	417 (7,650), 296 (59,600)$^{c)}$	0.36 0.1 M LiCl$^{f)}$	0.75	180
p-$CH_3CONHC_6H_4$	H	A	329–333 (DMF/ MeOH)	73	413 (7,080), 331 (11,080), 295 (23,500)$^{c)}$	0.35 0.1 M LiCl$^{f)}$	0.70	180
p-$CH_3C_6H_4$	H	G	250–256 (benzene/ MeOH)	60	411 (5,750), 332 (20,300), 262 (35,900)$^{c)}$	0.35 0.1 M LiCl$^{f)}$	0.76	93, 180
p-$C_6H_5C_6H_4$	H	A	321–323 (DMF)	84	418 (8,540), 331 (28,500), 299 (53,800)	0.40 0.1 M LiCl$^{f)}$	0.70	180

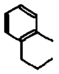
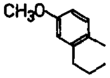
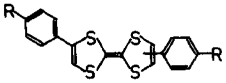
p-FC$_6$H$_4$	H	A	231–232 (benzene)	50	408 (4,480), 331 (14,900), 258 (36,640)$^{c)}$	0.40 0.1 M LiCl$^{f)}$	0.81	180
p-ClC$_6$H$_4$	H	G	245–251 (benzene/ MeOH)	50	424 (6,390), 330 (17,860), 269 (32,900)$^{c)}$	0.43 0.1 M LiCl$^{f)}$	0.79	93, 180
p-BrC$_6$H$_4$	H	G	249–255 (benzene/ MeOH)	33	400 (6,070), 331 (19,620), 272 (35,500)$^{c)}$	0.43 0.1 M LiCl$^{f)}$	0.79	93, 180
p-IC$_6$H$_4$	H	A	290–295 (DMF)	71	410 (6,740), 328 (21,000)$^{c)}$	0.42 0.1 M LiCl$^{f)}$	0.75	180
p-CH$_3$COOC$_6$H$_4$	H	A	228–230 (benzene)					65
m-CH$_3$COOC$_6$H$_4$	H	A	185–186 (EtOH)					65
C$_6$H$_5$	CH$_3$	G	145–154 (benzene/ MeOH)	50	484 (448), 381 (3,970), 290 (23,050)$^{c)}$	0.34 0.1 M LiCl$^{f)}$	0.73	180, 203
		A	209–211 (benzene)	91	485 (546), 406 (6,410), 279 (20,050)$^{c)}$	0.36 0.1 M LiCl$^{f)}$	0.72	61, 180
		F		90				92
		L						106
		A	211–213 (benzene)	75	472 (597), 396 (8,210) 284 (35,450)$^{c)}$	0.30 0.1 M LiCl$^{f)}$	0.68	61, 180
C$_6$H$_5$	C$_6$H$_5$	A	263 (CHCl$_3$/ acetone)	80	405 (3,600), 296 (20,500)$^{c)}$	0.41 0.1 M LiCl$^{f)}$	0.77	26, 180
		B Z = S (MeO)$_3$P		21	407 (4,470), 302 (29,800)$^{c)}$			66, 180
		G	268–270 (benzene/ MeOH)	50				93
		I Z = S M = Co$_2$ n = 8	262	25				99
		M R = Bu		50				97
		M		11				96
p-C$_4$H$_9$OC$_6$H$_4$	*p*-C$_4$H$_9$OC$_6$H$_4$	A	172					171
p-C$_8$H$_{17}$OC$_6$H$_4$	*p*-C$_8$H$_{17}$OC$_6$H$_4$	A	121					171

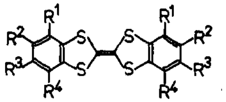
TABLE 5 (Continued)

R^1	R^2	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
p-$C_{10}H_{21}OC_6H_4$	p-$C_{10}H_{21}OC_6H_4$	A	127					171
p-$CH_3OC_6H_4$	CH_3	A	187–191 (MeCN)	67	485 (422), 370 (5,360), 307 (22,650)$^{e)}$	0.30 0.1 M LiCl$^{f)}$	0.71	180, 334
p-$CH_3C_6H_4$	CH_3	A	192–196 (MeCN)	82	482 (453), 370 (4,830)$^{e)}$	0.33 0.1 M LiCl$^{f)}$	0.75	180, 334
p-ClC_6H_4	CH_3	A	223–226 (benzene)	62	480 (463), 381 (4,220), 287 (26,870)$^{e)}$	0.38 0.1 M LiCl$^{f)}$	0.79	180, 334
p-BrC_6H_4	CH_3	A	212–215 (benzene)	73	480 (479), 385 (4,170), 289 (23,700)$^{e)}$	0.38 0.1 M LiCl$^{f)}$	0.78	180, 334
p-$C_6H_5C_6H_4$	CH_3	A	276–278 (DMF)	66	488 (840), 396 (5,780), 274 (41,400)$^{e)}$	0.37 0.1 M LiCl$^{f)}$	0.71	180
2-pyridyl	2-pyridyl	E	287–290 (THF)	80	425 (2,000), 385 (9,150), 355 (8,000)			89
$(CH_3)_3Si$	H	E	131–133	25				90
$(CH_3)_3Si$	$(CH_3)_3Si$	E	223–224 (hexane)	65				90



R	preparative method	K	S_G	S_C (°C)	N	I	E_1^{Ox}	E_2^{Ox}	references
liquid crystals									
C_4H_9	A B Z = O (EtO)$_3$P	136	145	–		191	0.43$^{k)}$	0.88	171, 335 335
C_8H_{17}	A	164	184	–		189			
$C_{10}H_{21}$	B Z = O (EtO)$_3$P	102	–	–		180	0.43$^{k)}$	0.89	335
C_4H_9O	A	171	186	–		210			171
$C_8H_{17}O$	A	146	156	172		–			171

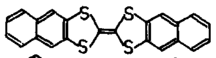
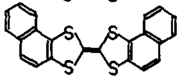
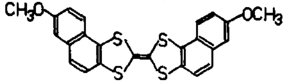
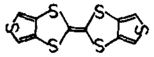
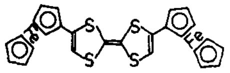
$C_{10}H_{21}O$	A	157	–	207	–	171
$C_5H_{11}COO$		186	195	–	–	171
$C_6H_{13}COO$		175	187	192	–	171
$C_7H_{15}COO$		174	182	214	–	171
$C_8H_{17}COO$		171	174	207	–	171
$C_9H_{19}COO$		165	165	205	–	171
$C_{10}H_{21}COO$		162	–	198	–	171
$C_{11}H_{23}COO$		160.5	–	200	–	171
$C_{12}H_{25}COO$		157	–	194	–	171

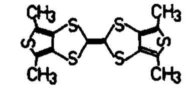
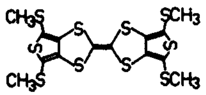
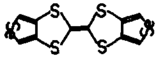
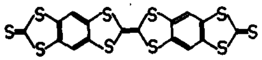


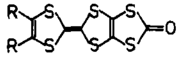
R^1	R^2	R^3	R^4	preparative method	m.p. (°C) (solvent)	yield (%)	λ_{max} (ε) (nm)	E_1^{Ox}	E_2^{Ox}	references
H	H	H	H	A	243 (benzene)	46	428 (297), 340 sh, 308 (20,700), 286 (18,400), 253 (20,600)[a]	0.72 0.1 M TEAT[g]	1.06	58
				A		80–90	436 (309), 310 (19,900), 289 (19,130)[c]	0.59 0.1 M LiCl[f]	0.89	57, 61, 180
				B Z = S (EtO)$_3$P	243	45	432 (400), 315, 296[v]	0.61 0.1 M TEAP	0.93	58, 70, 144 351
				G	242–243 (benzene/ MeOH)	30		0.71 0.2 M TBAT[k]	1.14	93, 142
				H		5–12				94, 95
				K		95				100
				M		25				96
CH_3	H	H	H	A	248–249 (pyridine)	94				60
H	CH_3	H	H	A	260–262 (pyridine)	67	432 (297), 343 sh, 311 (19,700), 287 (18,200), 256 (17,800)[a]	0.68 0.1 M TEAT[g]	1.02	58, 60
				A	253	44				59
				B Z = S (EtO)$_3$P	262 (benzene)	25	436 (417), 318, 294[v]			58, 351

TABLE 5 (Continued)

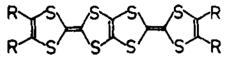
R^1	R^2	R^3	R^4	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
				H	260–262 (pyridine)	33				47
				K		86				100
H	CH_3	CH_3	H	B Z = S $(EtO)_3P$	> 360 (DMF)	45	427 (525), 316 (316 (13,200), 293 (12,000)[v]			351
H	Cl	H	H	A	315–318 (pyridine)	88				60
H	I	H	H	A	303–304 (pyridine)	95				60
H	NO_2	H	H	A	360–366 (pyridine)	60				60

R	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
	A	> 400	88				60
	A	302–303 (benzene)	61	375 (2,870), 321 (21,650), 294 (41,250)[e]	0.52 0.1 M LiCl[f]		61, 180
	A	279–284 (benzene)	27	397 (3,030), 323 (22,550), 292 (45, 850)[e]	0.49 0.1 M LiCl[f]	0.85	61, 180
	A	259–260 (CH_2Cl_2/hexane)	31		0.70		48, 336
	B Z = Se $(MeO)_3P$ Z = O,S $(RO)_3P$		 58 –				 48 48
	B Z = Se $(MeO)_3P$	> 300 ($CHCl_3$)	31				337

	B Z = Se Ph_3P	295–297 (CCl_4)	60				49, 50
	B Z = Se $(MeO)_3P$	183–184 ($CHCl_3$)	45		0.87 0.1 M TBAP	1.16	353
	B Z = S $(MeO)_3P$	260–263	54				354
	B Z = S $(EtO)_3P$		42				355



R							
$COOCH_3$	B	215–220	18	430 (1,410), 295 (20,000), 260 (12,9000), 238 (17,800)w)	0.89 TEAP	0.98	338
CN	B	196 (MeCN)					161
CF_3	B	146–147 (hexane)					161



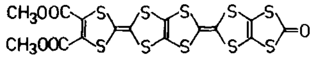
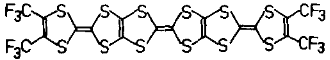
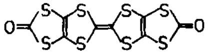
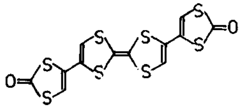
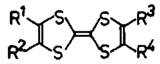
R	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
CN	B	290 dec. ($CHCl_3$)					161
CF_3	B	233–235 (benzene)					161
	B	265–270 dec.	3	440 (1,380), 310 (19,500), 280 (15,850), 239 (16,600)w)	0.78 TEAP	0.92	338
	B	252 dec. (PhCl)					161
	B	> 360	76				44, 163, 164
		275–277		410, 325, 295w)	0.73 0.1 M TEAPq)	0.90	339

TABLE 5 (Continued)



R^1	R^2	R^3	R^4	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
H	H	CH_3	CH_3	A	117–119 (MeCN)	78	445 (640), 360 sh, 322 sh, 308 sh, 299 (14,300), 290 sh, 278 sh$^{b)}$	0.28 0.05 M TBAT	0.65	82, 323
H	H	$-(CH_2)_3-$		A	139 sublim.			0.20 $NaClO_4$	0.54	340
H	H	$-(CH_2)_4-$		C	105–106	41	460 (260), 364 (1,500), 322 (9,550), 310 (9,800), 299 (10,500)			75
CH_3	CH_3	$-(CH_2)_3-$		A	232			0.26 0.1 M TBAT	0.61	83, 341
CH_3	CH_3	$-(CH_2)_4-$		C C	174–175 194	43	478 (214), 323 (9,550), 314 (10,500), 298 (11,200), 286 (10,200)	0.32 0.1 M TBAP$^{v)}$		75, 356
CH_3	C_2H_5	$-(CH_2)_3-$		A	132 sublim.			0.16 $NaClO_4$	0.52	340
CH_3	CH_3	H	$C_{17}H_{35}$	A	82–83 (MeCN)		480 (447), 320 (11,700), 310 (12,300), 300 (12,900)$^{b)}$			326
CH_3	CH_3	$C_{16}H_{33}$	$C_{17}H_{35}$	A	82–83		490 (159), 313 (14,800), 300 (14,500)$^{b)}$			326
CH_3	CH_3	$C_{17}H_{35}$	$C_{17}H_{35}$	A	80–81		485 (240), 360 sh, 323 sh, 312 (11,000), 300 (11,000)$^{b)}$			326
H	H	$-S-(CH_2)_2-S-$		A				0.39 0.1 M TEAP	0.69	81
H	H	$-S-(CH_2)_3-S-$		A				0.41 0.1 M TEAP	0.73	81
CH_3	CH_3	$-S-(CH_2)_2-S-$		A B	169–170 (benzene)	 9	459 (660), 340 (10,000), 312 (11,750)$^{v)}$	0.37 0.1 M TEAP	0.67	81, 351
CH_3	CH_3	$-S-(CH_2)_3-S-$		C		62		0.36 0.1 M TEAP	0.69	81
$-(CH_2)_3-$		$-S-(CH_2)_2-S-$		A				0.37 0.1 M TEAP	0.66	81

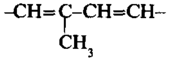
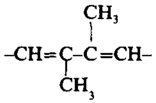
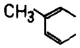
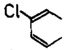
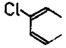
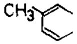
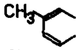
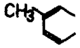
CH_3S	CH_3S	$-S-(CH_2)_2-S-$		A				0.48 0.1 M TEAP	0.72	81
CH_3S	CH_3S	$-S-(CH_2)_3-S-$		A				0.48 0.1 M TEAP	0.73	81
$-S-(CH_2)_2-S-$		$-S-(CH_2)_3-S-$		C		22		0.49 0.1 M TEAP	0.77	81
$-CH=CH-CH=CH-$		$-S-(CH_2)_2-S-$		B	225–226	14	420 (390), 331 (12,300),			351
 $-CH=C(CH_3)-CH=CH-$		$-S-(CH_2)_2-S-$		B	195–197 (benzene)	2	439 (515), 331 (9, 350), 306 (11,500)[v]			351
 $-CH=C(CH_3)-C(CH_3)=CH-$		$-S-(CH_2)_2-S-$		B	243 (pyridine)	5	442 (600), 334 (12,900), 310 (14,500)[v]			351
CH_3S	CH_3S	$COOCH_3$	$COOCH_3$		88–90 (MeCN)					161
CH_3	CH_3	H	$COOCH_3$	C	132–134 (MeCN)	21	438 (1,860), 313 (11,500), 292 (11,200)			77
CH_3	CH_3	CN	CN		230	20				167
H	H	$-(CH=CH)_2-$			138–140	68	444 (100), 313 (16,200), 294 (15,800)[d]	0.40	0.75	84
				C	135–136	40				75
CH_3	CH_3	$-(CH=CH)_2-$		C	190–191	30	454 (316), 319 (12,900), 292 (14,100), 260 (10,000), 253 (8,700), 247			75
				K		89				100
$-(CH_2)_4-$		$-(CH=CH)_2-$		C	207–208	31	456 (190), 319 (9,750), 307 (10,000), 293 (11,000), 281, 271, 265, 258			75
$COOCH_3$	$COOCH_3$	$-(CH=CH)_2-$		B Z = S Z = Se	173–174	 3 31	416 (100), 313 (17,400), 255 (19,100)[n]			84
				H	207–210 (pyridine/H_2O)	15				47
				K		75				100
				K		98				100
				K		82				100

TABLE 5 (Continued)

R^1	R^2	R^3	R^4	preparative method	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
H	H	H	C_6H_5	A	78–81 (hexane)		400 (2,820), 322 (12,500), 302 (14,100), 277 (13,900), 228	0.35 0.05 M TBAT	0.70	276, 323
H	H	H	p-$BrCH_2CH_2C_6H_4$	A	128–133 (c-C_6H_{12})					276
H	H	H	p-$CH_2=CHC_6H_4$		100–104 (c-C_6H_{12})			0.33 0.05 M TBAT	0.70	276, 323
H	H	H	p-$CH_3COOC_6H_4$	A	125–127 (MeCN)	70				169
H	H	H	p-HOC_6H_4		122–124 ($EtOH/H_2O$)	96				169
H	H	H	COCl		130–135 (hexane)	90				173
H	H	H	$CON(CH_3)_2$		162–163	18				159
CH_3	CH_3			K		81				100
$-(CH_2)_3-$				K		40				100
H	H	H	NCO		75–78 (benzene/ hexane)	80				173
H	H	H	$NHCOOC_6H_4NO_2$-p		154–155 (benzene/ hexane)	86	371 (4,700), 350 (5,500), 310 (14,800), 272 (20,400)$^{a)}$			173
H	H	H	COOH		182–184 (benzene)	60	420 (100), 313 (7,100), 301 (6,900)$^{c)}$	0.47 0.1 M TEAP	0.83	175
H	H	H	$COOC_2H_5$		79.5–80.5 (MeOH)	50	424 (1,920), 314 (13,600), 303 (12,900), 292 sh$^{a)}$	0.47 0.1 M TEAP	0.83	175
H	H	H	CHO		110–111 (isooctane)	44	462 (2,260), 312 (12,900), 298 (13,300), 285 (13,300)$^{a)}$	0.53 0.1 M TEAP	0.89	175
H	H	H	$CH=CH_2$		32 (hexane)			0.42 0.1 M TEAP	0.77	174, 342
H	H	H	$COCH_3$		152–153 (isooctane)	67	455 (1,940), 312 (10,200), 300 (9,800), 285 (9,600)$^{a)}$	0.47 0.1 M TEAP	0.83	175

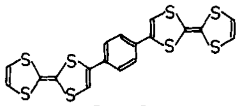
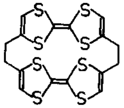
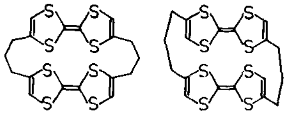
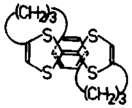
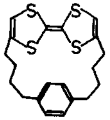
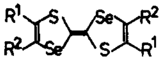
H	H	H	CH_3					0.33 0.1 M TEAP	0.70	175
H	H	H	CH_2OH		70–71 (isooctane/ (toluene)	34	452 (244), 353 (2,300), 316 (13,400), 309 (13,200)$^{a)}$	0.41 0.1 M TEAP	0.79	175
H	H	H	C_2H_5					0.33 0.1 M TEAP	0.70	175
H	CH_3	H	$COOC_2H_5$		67–70 (isooctane)	35	432 (1,500), 313 (12,000), 303 (11,400), 294 (11,000)$^{a)}$	0.45 0.1 M TEAP	0.81	175
H	CH_3	CH_3	$COOC_2H_5$		62–64 (hexane)		415 (1,300), 319 (9,600), 310 (9,200), 289 (8,900)$^{a)}$	0.43 0.1 M TEAP	0.79	175
H	H	$COOC_2H_5$	$COOC_2H_5$		63 (isooctane)	33	460 (1,060), 314 (19,500), 302 (18,750), 292 (17,700)$^{a)}$	0.57 0.1 M TEAP	0.91	175
H	CH_3	$COOC_2H_5$	$COOC_2H_5$		33–34 (hexane)		447 (1,450), 316 (13,800), 293 (13,700)$^{a)}$	0.54 0.1 M TEAP	0.87	175
				A	242	21	440 (4,020), 320 (21,600), 310 (19,800)$^{f)}$	0.35 0.05 M TBAP	0.76	323, 343
				A	> 210	15				344
 mixture of isomers				A		9				344
				A	180–182 (c-C_6H_{12})					345
				A	157–158	63				345

TABLE 6

Molecular properties of DSDTF (redox potential in acetonitrile vs. sce)



R^1	R^2	Z	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
H	H		118	25	470 (200), 375 (980), 325 (5,900), 297 (9,800), 282 (9,100), 235 (3,700)[b]	0.40 0.1 M TEAP	0.72	71, 107, 108, 178
		Se	117 (hexane)	60–80				71, 107
CH_3	H	Se	123–125 (hexane)	60	490 (200), 370 (2,500), 295 (21,000), 240 (6,200)[b]			73
CH_3	CH_3	Se			495 (172), 327 (953), 298 (13,980)	0.33 TBAT	0.68	109
$-(CH_2)_3-$		Se $(EtO)_3P$	244 dec.	37	472 (257), 433 (204), 347 (3,100), 334 (5,900), 305 (10,700)[n]			110
$-CH_2-CH(CH_3)-CH_2-$		S $(MeO)_3P$	160–163 (hexane)	5	475 (159), 340 sh, 310 (14,100)[m]	0.39 0.1 M TEAP	0.70	28
		Se $(MeO)_3P$						28
$-(CH_2)_4-$		S $(EtO)_3P$	sublim.	11		0.28 TEAP	0.63	113
$-(CH{=}CH)_2-$		S $(EtO)_3P$	247–248	4	448 (230), 315 (9,800), 284 (15,100), 254 (19,000)[a]			110
		Se $(EtO)_3P$		39				110
$COOCH_3$	$COOCH_3$	Se Ph_3P	138 (MeOH)	50	434 (2,750), 325 (10,700), 290 (26,900) 250 (24,500)			108, 114
COOH	COOH		> 280					108, 114, 134

TABLE 7

Molecular properties of TSF (redox potential in acetonitrile vs. sce)

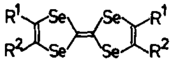
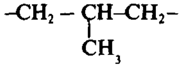
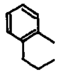
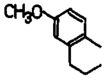
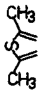
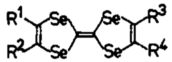
 R^1	R^2	Z	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
H	H	Se $(MeO)_3P$ or Ph_3P	133 (hexane)	60–80	495 (130), 365 (1,400), 300 (12,300), 287 (14,200)$^{b)}$	0.48 0.1 M TEAP	0.76	71, 119, 178, 204
CH_3	CH_3	S $(EtO)_3P$	250 dec.	30	508 (200), 299 (12,600)$^{k)}$	0.44 0.1 M TEAP	0.72	28, 123
		Se $(EtO)_3P$			500 (152), 365 (1,600), 304 (16,200)	0.54 0.2 M TBAT$^{k)}$	0.93	28, 128, 129, 327
					534 (176)$^{u)}$	0.42 TBAA$^{e)}$	0.81	141
						0.43 0.1 M TBAT$^{k)}$	0.73	134
CD_3	CD_3	Se $(MeO)_3P$		90	508, 299$^{k)}$	0.43 0.1 M TBAT$^{k)}$	0.73	134
$-(CH_2)_3-$		Se $(EtO)_3P$	207–209 (PhCl)	30–60	498 (166), 370 (1,250), 301 (13,800)	0.55 0.2 M TBAT$^{k)}$	0.92	120, 128, 129, 327
					493 (230), 350 sh, 310 sh, 303 (16,600)$^{m)}$			28
 $-CH_2-\underset{CH_3}{CH}-CH_2-$		Se $(MeO)_3P$	181–184 (hexane)	60	498 (210), 350 sh, 303 (16,200)$^{m)}$	0.48 0.1 M TEAP	0.75	28
$-CH_2-S-CH_2-$		Se $(EtO)_3P$	228–230	10	495 (525), 438 (500), 317 (8,300)$^{e)}$			137
$COOCH_3$	$COOCH_3$	Se Ph_3P	144–145 (MeOH/benzene)	75	422 (10,000), 328 (5,000), 285 (2,700), 260 (24,600), 212 (14,500)			168
$-(CH=CH)_2-$		Se	291–293	66	470 (158), 320 (5,000), 286 (16,200),	0.78	1.17	138, 142

TABLE 7 (Continued)

R^1	R^2	Z	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
		Ph_3P			221 (28,200)[a/c]	0.2 M TBAT[k]		
		Se Ph_3P	288–291 (CCl_4)	65				139
	$-S-(CH_2)_2-S-$	O $(EtO)_3P$	220	–				68
		Se $(EtO)_3P$	–					68
	$-Se-(CH_2)_2-Se-$	O $(EtO)_3P$	235–240	10		0.94 0.1 M TBAP[v]		118, 350
		Se $(RO)_3P$		–				
	cis							
	trans	Se $(EtO)_3P$	228–230 (DMF)	15	505 (243), 365 (8,100), 318 (18,200), 281 (25,800)[c]	0.50 0.1 M LiCl[q]		115
	cis	Se $(EtO)_3P$	242–245 (DMF)	22	505 (255), 365 (8,350), 317 (20,350), 281 (26,800)[c]	0.49 0.1 M LiCl[q]		115
	trans	Se $(EtO)_3P$	235–236 (DMF)	34	510 (238), 362 (10,200), 321 (19,100), 283 (30,700)[c]	0.48 0.1 M LiCl[q]		115
		Se $(EtO)_3P$	240–243 (DMF)	27	510 (243), 362 (10,800), 325 (19,500), 283 (32,400)[c]	0.47 0.1 M LiCl[q]		115
$(CH_3)_3Si$	$(CH_3)_3Si$		104–105 (hexane)	20				90
		Se $(RO)_3P$		–				48
		Se Ph_3P	313–315 (CCl_4)	40				49, 50



R¹	R²	R³	R⁴	Z	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
H	H	–(CH$_2$)$_3$–		Se (MeO)$_3$P	153			0.52 0.1 M TBAP$^{v)}$	0.88	341, 357
CH$_3$	CH$_3$	–(CH$_2$)$_3$–		Se (MeO)$_3$P	257			0.48 0.1 M TBAP$^{v)}$	0.87	346
H	H	H	COOH		165			0.63 0.1 M TEAP	0.90	331
CH$_3$	CH$_3$	–(CH$_2$)$_4$–		Se (MeO)$_3$P	212			0.5 0.1 M TBAP$^{v)}$		356
H	H	CH$_3$	CH$_3$	Se (MeO)$_3$P	137–138			0.52 0.1 M TBAP$^{v)}$	0.89	357

TABLE 8

Molecular properties of TTeF (redox potential vs. sce)

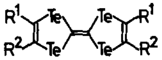
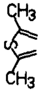
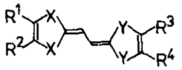
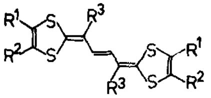
 R^1	R^2	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
$-(CH_2)_3-$		260 (PhCl)	32	610 (189), 410 (9,115), 335 (19,350), 320 (15,560)[v]	0.40 TBAA[e]	0.69	141, 347
$-(CH=CH)_2-$			10		0.71 0.2 M TBAT[k]	1.05	142
		295–298 ($ClCH_2CHCl_2$)	75		0.78 TBAT[k]	1.20	143

TABLE 9

Molecular properties of vinylogous TTF and TSF (redox potential in acetonitrile vs. sce)

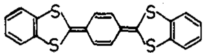
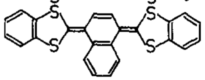
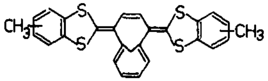
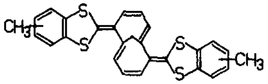


R^1	R^2	R^3	R^4	X	Y	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E_1^{Ox}	E_2^{Ox}	references
H	H	H	H	S	S	164–165	83	406 (21,400), 387 (20,400)[w]	0.20 0.1 M TEAP	0.36	79
CH_3	CH_3	CH_3	CH_3	S	S	220–222	78	415 (29,500), 394 (28,200)[w]			79
$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	S	S	184–185	73	389 (26,300), 374 (28,200)[w]			79
H	H	$-(CH{=}CH)_2-$		S	S	126–127	37	400 (13,800), 380 (15,500)[w]			79
$COOCH_3$	$COOCH_3$	$-(CH{=}CH)_2-$		S	S	134–135	46	393 (33,900), 374 (36,300)[w]			79
$-(CH{=}CH)_2-$		$-(CH{=}CH)_2-$		S	S	220	48	394 (33,900), 376 (35,500)[w]	0.47 0.1 M TEAP	0.64	144, 146
						225	80	392 (87,100), 374 (64,600)[a]	0.26 e)	0.41	147
H	H	H	H	S	Se	162	61	398 (12,900), 372 (14,500)[w]	0.26 0.1 M TEAP	0.40	145
$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	S	Se	175–176	94				145
H	H	H	H	Se	Se	183–184	68	390 (11,500), 365 (11,500)[w]	0.33 0.1 M TEAP	0.47	145
$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	Se	Se	156–157	60				145



R^1	R^2	R^3	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E^{Ox}	references
H	H	H	118–120	55		0.22 0.1 M TEAP	144
H	H	C_6H_5	171–172	45		0.28 0.1 M TEAP	144

TABLE 9 (Continued)

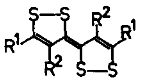
R^1	R^2	R^3	m.p. (°C) (solvent)	yield (%)	$\lambda_{max}(\varepsilon)$ (nm)	E^{Ox}	references
$-(CH=CH)_2-$		H	225–227	69		0.47 0.1 M TEAP	144
$COOCH_3$	$COOCH_3$	H	195–197 ($MeNO_2$)	42			144
COC_6H_5	COC_6H_5	H	203–205 ($MeNO_2$)	60			144
$COOCH_3$	$COOCH_3$	C_6H_5	212–216 ($MeNO_2$)	80			144
COC_6H_5	COC_6H_5	C_6H_5	244–246	51			144
			280	38	503 (91,100), 478 (64,500)[u]	0.27 0.1 M TBAHP[x,g]	152, 153, 348
						0.27 0.1 M TBAHP[x,g]	155, 348
			152–154	66	460 (11,500), 384 (12,900)[k]		156
			166–168	95	494 (17,720), 316 sh, 271 sh	0.32 0.1 M TBAHP[x,g]	156

a) in acetonitrile, b) in hexane, c) in tetrahydrofuran, d) in cyclohexane, e) in benzonitrile, f) in methanol/benzene (4:1, v:v), g) vs. Ag/AgCl electrode, h) vs. Ag/$AgNO_3$ (0.01 M) electrode, i) probably *trans*-isomer, k) in methylene chloride, l) in benzene, m) in chlorobenzene, n) in 1,2-dichloroethane, o) in 0.1 N resp. 0.01 N sodium hydroxide, p) in ethanol, q) in *N,N*-dimethylformamide, r) in isooctane, s) in methanol, t) in dioxan, u) in carbon disulfide, v) in 1,1,2-trichloroethane, w) in chloroform x) in propionitrile.

TBAA: tetrabutylammonium hexafluoroarsenate, TBAHP: tetrabutylammonium hexafluorophosphate, TBAP: tetrabutylammonium perchlorate, TBAT: tetrabutylammonium tetrafluoroborate, TEAP: tetraethylammonium perchlorate, TEAT: tetraethylammonium tetrafluoroborate.

TABLE 10

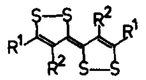
1,2-TTF by dehydrogenation of the corresponding dihydro compounds *171*.[316]



R^1	R^2	oxidation agent	solvent	yield (%)
Ph	Ph	DDQ	benzene	49
		SeO_2	CH_2Cl_2	46
H	Ph	air	acetone	4
		$PhI(OAc)_2$	$CHCl_3$	26–29
		SeO_2	CH_2Cl_2	67

TABLE 11

1,2-TTF by reduction of the corresponding 3*H*-1,2-dithiolium salts *135* and *136* and their properties.[316]



R^1	R^2	reducing agent	solvent	yield (%)	m.p. (°C) (solvent)	λ_{max}(solvent) (nm)
Ph	H	$TiCl_3$$^{b)}$	THF	10	179–180$^{a)}$ 180–181$^{a)}$	
		$TiCl_3$$^{b)}$	diglyme	20		
		$TiCl_3$$^{c)}$	THF	3		
Ph	Me	Zn$^{b)}$	MeCN	59	143–144 ($CHCl_3$)	
Ph	Ph	Zn$^{b)}$	CH_2Cl_2	29	228.5 (CH_2Cl_2/MeOH)	497 ($CHCl_3$)
		Zn$^{b)}$	MeCN	46		502 (CCl_4)
		Ag$^{b)}$	CH_2Cl_2	13		502 (c-C_6H_{12})
		$TiCl_3$$^{b)}$	MeCN	38		526 (CS_2)
		Zn/$Br_2$$^{c)}$	EtOH	36		
-(CH=CH)$_2$-		Zn$^{b)}$	MeCN	1.5	147–149$^{a)}$ (CH_2Cl_2/MeOH)	
		Zn$^{b)}$	DMF	41		
					212–213$^{a)}$ (CH_2Cl_2/MeOH)	

a) m.p. in each case of one isomer, b) reduction of the dithiolium salt 135, c) reduction of the dithiolium salt 136

TABLE 12

1,2-TTF by reaction of triethyl phosphite with 1,2-dithiole-3-thiones ***132***.[313a]

Figure 95

RR^1	**R^2**	**Yield (%)**	**m.p. (°C) (solvent)**	**λ_{max}(solvent) (nm)**
CH_3S	CH_3S	30	198$^{a)}$ (CH_2Cl_2)	481, 440 sh, 350 (CH_2Cl_2)
		45	238$^{a)}$ (CH_2Cl_2)	473, 454 sh, 375 (CH_2Cl_2)
$-S-CH_2-S-$		35	181 (DMF/MeCN)	580, 540 sh, 370 (MeCN)
$-S-(CH_2)_2-S-$		38	177	580 sh, 550, 400 (CH_2Cl_2)

a) m.p. in each case of one isomer

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