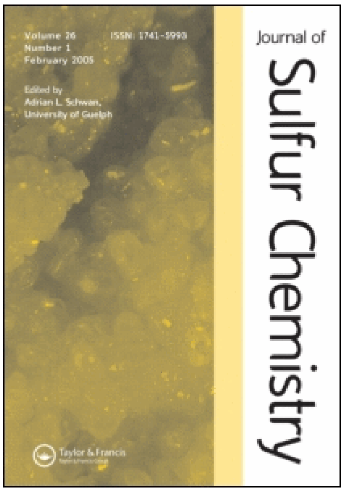

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Synthesis, Reactions, and Selected Physico-Chemical Properties of 1,3- and 1,2-tetrachalcogenafulvalenes

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

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This review describes the synthesis of 1,3- and 1,2-tetrachalcogenafulvalenes, 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. For selected charge-transfer complexes of tetrachalcogenafulvalenes, the relation between molecular structure and solid-state structure, respectively, and electric conductivity are discussed. Superconducting properties of some charge-transfer complexes with tetrachalcogenafulvalenes as donor are reported.

Preparations of important starting compounds for the synthesis of tetrachalcogenafulvalenes (such as 1,2- and 1,3-dithiole, 1,3-thiaselenole, and 1,3-diselenole derivatives) have been considered in this review.

Selected properties (melting point, UV–Vis absorption data and oxidation potentials) of 1,2- and 1,3-tetrachalcogenafulvalenes are summarized in appropriate tables.

Keywords: Tetrachalcogenafulvalenes; CT complexes; TTF; polymeric TTF

CONTENTS

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*Corresponding author.

†Appendices A and B, comprising tables A1, B1–B6, can be found at the website (http://www.taylorandfrancis.metapress.com/openurl.asp?genre = article&issn = 1029-0508&volume = 24&issue = 01&page = 01&sm = appendix1; http://www.taylorandfrancis.metapress.com/openurl.asp?genre = article&issn = 1029-0508&volume = 24&issue = 01&page = 01&sm = appendix2).

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INTRODUCTION

Tetrachalcogenafulvalenes are electron donors which form charge-transfer (CT) complexes with electron acceptors such as tetracyanoquinodimethane (TCNQ), halogens or metal salts. They can also be easily oxidized electrochemically to form radical salts. Among them are those of special interest which possess a segregated stack structure. They are so-called organic metals. 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, has strongly stimulated efforts to find efficient preparations for tetrachalcogenafulvalenes and also for the corresponding starting materials. Especially, heteroatoms have been introduced at peripheral sites in the donors, and conjugated tetrachalcogenafulvalenes with extended π-systems have been prepared. It is known that a strong inter-stack as well as intra-stack interaction in CT complexes leads to an increased dimensionality and inhibits Peierls transitions at low temperatures.

Therefore many efforts have been made to synthesize donors for organic superconductors with heteroatoms in the outer sphere of the tetrachalcogenafulvalene framework.

Interest in the preparation of vinylogous derivatives of tetrachalcogenafulvalenes with conjugation between dichalcogenole rings is founded on the fact that increased separation of the dichalcogenole rings decreases the Coulomb repulsion in the dicationic state and improves the electrical transport properties of organic conductors.

The high conductivity of tetrachalcogenafulvalene complexes is, however, exhibited by single crystals and this places limitations on their practical application. Hi gh interest and intensive research on tetrachalcogenafulvalenes led to significant advances in synthetic chemistry of tetrachalcogenafulvalenes, especially tetrathiafulvalenes (TTF). Now the TTF moiety can be easily prepared from cheap starting materials in reasonable quantities and can be modified by various synthetic strategies. This development allowed the utility of the TTF building block for alternative ways of organizing assemblies of TTF derivatives in the chemistry of materials, such as incorporating TTF moieties into macrocyclic or supramolecular compounds (e.g. crown-annelated ligands, dendrimers, rotaxanes, cyclophanes), self-assembled monolayers or Langmuir–Blodgett film deposition and preparation of mesogenic compounds or intramolecular charge-transfer complexes, which can be used as cation sensors, nonlinear optical materials, supramolecular switches or devices, organic ferromagnets, photochromic materials and redox polymers.

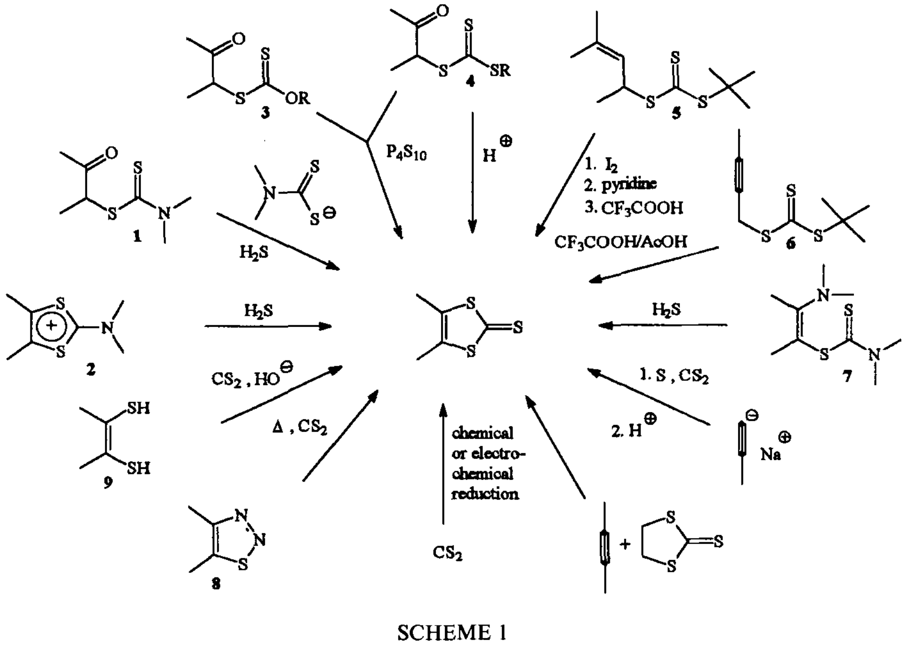
The relations between structures of tetrachalcogenafulvalenes and their properties as well as other aspects have been the object of international conferences [1–30], reviews [31–65], and books [66–81].

In this review a survey of methods for the preparation of tetrachalcogenafulvalenes and their properties is given.

1. SYNTHESIS OF TETRATHIAFULVALENES (TTF)

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

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.



SCHEME 1

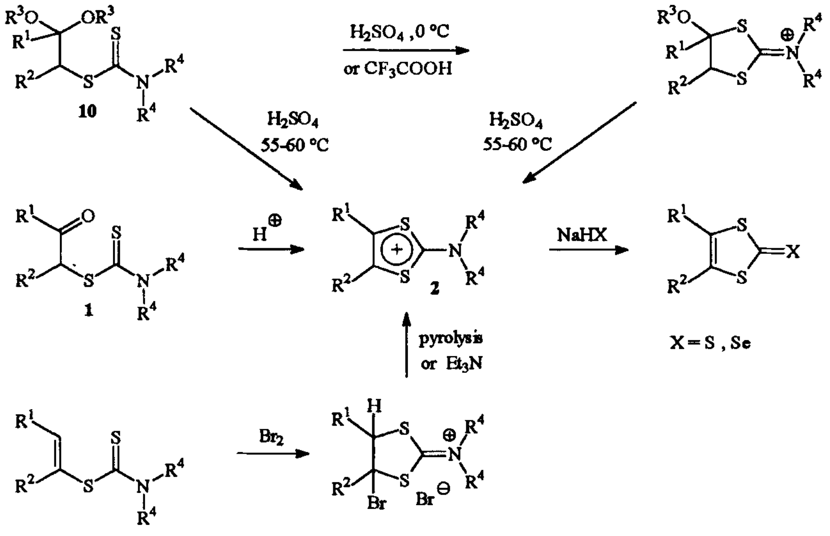
With a large variety of substituents the cyclization of β-keto *N,N*-dialkyldithiocarbamates **1** with concentrated sulfuric acid or 70% perchloric acid and subsequent treatment of the so formed 2-amino-1,3-dithiolium salts **2** with hydrogen sulfide in pyridine or methanol gives high yields [82–84].

The corresponding β-keto *N,N*-dialkyldithiocarbamate **1** is cyclized directly to e.g. 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%) [85].

Cyclization of β-keto *N,N*-dialkyldithiocarbamates **1** with concentrated sulfuric acid to 2-(*N,N*-dialkylamino)-1,3-dithiolium salts is also successful in the case of β-formyl *N,N*-dialkyldithiocarbamates **10** [86,87]. In the actualized form cyclization in sulfuric acid at 55–60°C affords the 2-(*N,N*-dialkylamino)-1,3-dithiolium salts **2**, which can be converted into the 1,3-dithiole-2-thione or 1,3-dithiole-2-selone by treatment with sodium hydrogen sulfide or sodium hydrogen selenide, respectively.

If the cyclization is accomplished at 0°C or with refluxing trifluoroacetic acid, only intermediate alkoxy substituted dithiolium salts are formed. These compounds provide the desired 2-(*N,N*-dialkylamino)-1,3-dithiolium salts upon treatment with sulfuric acid at 55–60°C.

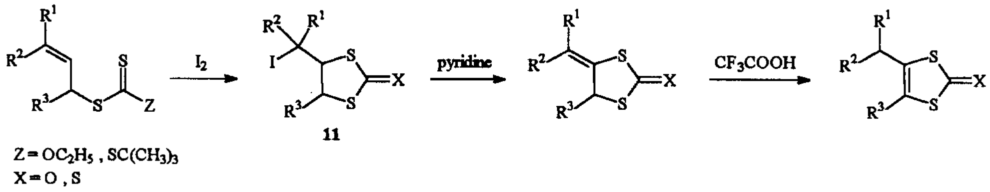
Oxidative cyclization of alkenyl *N,N*-dialkyldithiocarbamates with bromine in dichloromethane or chloroform gives rise to the iminium bromides as stable compounds. The 2-(*N,N*-dialkylamino)-1,3-dithiolium salts **2** can be obtained by treatment of the iminium bromides with triethylamine [88], but cleaner products with higher yields are synthesized by thermal elimination of hydrogen bromide under reduced pressure [89–94]. The cyclization and dehydrobromination sometimes proceeds in one step [95].



SCHEME 2

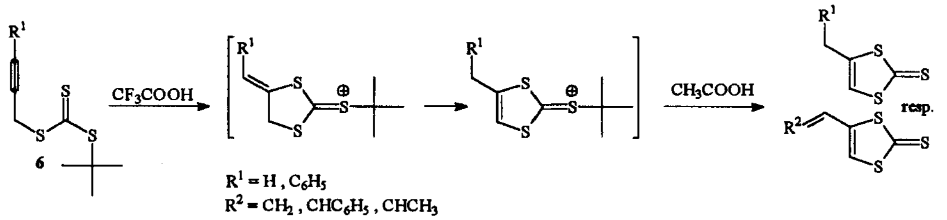
The cyclization of β-keto *O*-alkyldithiocarbonates **3** or β-keto *S*-alkyl trithiocarbonates **4** succeeds with phosphorus pentasulfide in boiling decaline (Scheme 1) [96–101]. In the case of β-keto *S*-*t*-butyl trithiocarbonates **4** the cyclization takes place in higher yields with a mixture of trifluoroacetic acid and acetic acid [102].

The readily available allyl halides can be easily converted with high yields into variously substituted 1,3-dithiol-2-ones or 1,3-dithiole-2-thiones with potassium ethyl xanthate or sodium *t*-butyl trithiocarbonate in a multistep reaction. The corresponding allyl *O*-ethyl dithiocarbonate or allyl *t*-butyl trithiocarbonate **5** is cyclized with iodine with concomitant loss of ethyl iodide or isobutylene/hydrogen iodide. In the next steps elimination of hydrogen iodide from the 1,3-dithiolane-2-thione **11** with pyridine and isomerization of the double bond with trifluoroacetic acid occurs [103].



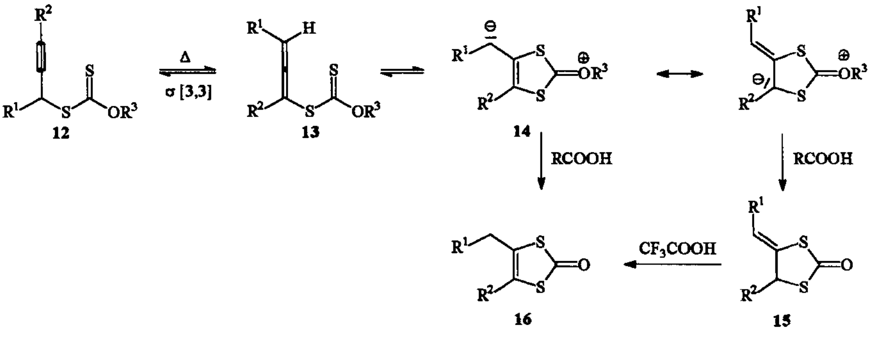
SCHEME 3

In a similar manner, 1,3-dithiole-2-thiones are formed in high yield in a one-step reaction by ring closure of propargyl *t*-butyl trithiocarbonate **6** with trifluoroacetic acid in glacial acetic acid. When acetylenic alcohols ($R^1 = R^2CHOH$) are employed in the reaction sequence dehydration occurs, resulting in the formation of vinyl-1,3-dithiole-2-thiones [104].



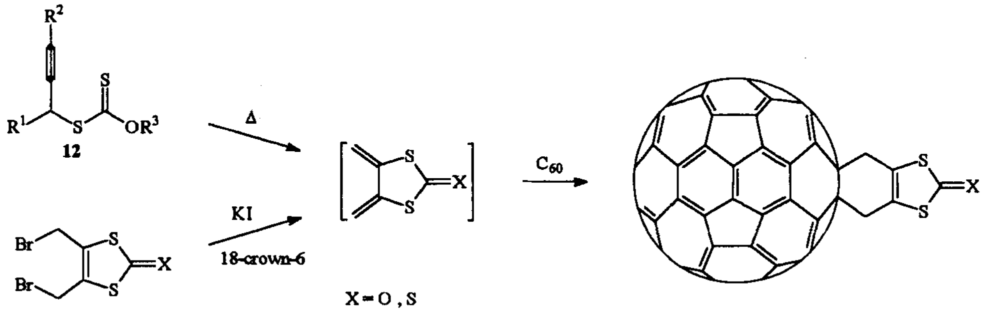
SCHEME 4

Upon heating, propargyl xanthates **12** undergo a thermal sigmatropic rearrangement to provide the corresponding *S*-allenyl xanthates **13**, which are probably in equilibrium with the betaines **14**. These reactive intermediates give with carboxylic acids in chlorobenzene the corresponding 1,3-dithiol-2-ones **15** and/or **16**. The 1,3-dithiol-2-ones **15** can be easily isomerized to the thermodynamic stable **16** with hot trifluoroacetic acid [105]. The so formed 1,3-dithiol-2-ones are isomeric to those synthesized by cyclization of allyl *O*-ethyl dithiocarbonates with iodine.



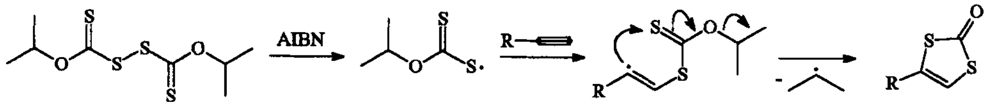
SCHEME 5

In a [4 + 2]cycloaddition of 4,5-bis(methylene)-1,3-dithiol-2-one or -thione, prepared by a thermal rearrangement of a propargyl xanthate **12** ($R^1 = H$, $R^2 = CH_2OCOC_6H_5$, $R^3 = CH_3$) or by treatment of 4,5-bis(bromomethyl)-1,3-dithiol-2-one or -thione with potassium iodide in the presence of 18-crown-6, to C_{60}, a C_{60} functionalization with a 1,3-dithiol-2-one or-thione structure is achieved [106,107].



SCHEME 6

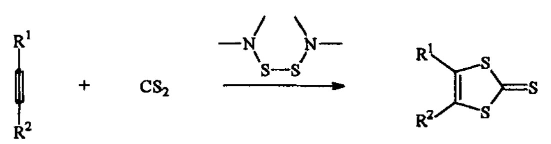
Thermolyse of diisopropyl xanthogen disulfide, initiated by AIBN, affords in the presence of an alkyne in a one step reaction the corresponding 1,3-dithiol-2-ones. After cleavage of the S–S bond the addition of the thiyl radical to the alkyne is expected forming a vinyl radical, which could cyclize by extruding an isopropyl radical [108].



SCHEME 7

Enamines can be substituted in the 2-position by tetramethylthiuram disulfide in the presence of triethylamine and the products **7** cyclized by passing hydrogen sulfide through the reaction mixture (Scheme 1). Enamines of cyclic or aryl substituted ketones give 1,3-dithiole-2-thiones in good yields (35–90%). Enamines of aliphatic aldehydes do not react. With ketimines of acyclic dialkyl ketones the reaction occurs. However, the yields of 1,3-dithiole-2-thiones are moderate (10–35%) [85].

The reaction between alkynes 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 [109].



R_1	C_6H_5	t-C_4H_9	C_6H_5	H	$COOCH_3$
R_2	H	H	$COOC_2H_5$	$COOCH_3$	$COOCH_3$

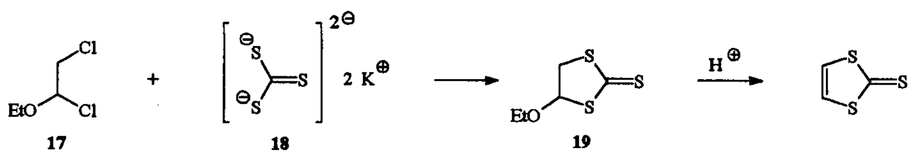
SCHEME 8

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 in liquid ammonia

[110]. Experimental modification of this conversion (reaction in THF with *n*-BuLi at −78°C, subsequently with sulfur at 0°C and then with carbon disulfide at −90°C) provides a higher yield (82%) and enables the extension to monosubstituted alkynes [111–115].

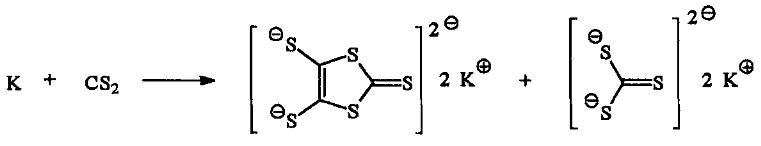
Higher yields of unsubstituted 1,3-dithiole-2-thione are obtained in the reaction of dimethyl acetylenedicarboxylate with 1,3-dithiolane-2-thione, followed by hydrolysis and decarboxylation of the 4,5-bis(carbomethoxy)-1,3-dithiole-2-thione formed [116]. The reaction of alkynes with 1,3-dithiolane-2-thione proceeds only in the case of alkynes with electron-withdrawing substituents (COOR, CF_3, CN, CHO) [117–119].

A good yield of unsubstituted 1,3-dithiole-2-thione is obtained in a two-step synthesis, starting from 1,2-dichloroethyl ethyl ether **17** and potassium trithiocarbonate **18**. The 4-ethoxy-1,3-dithiolane-2-thione **19** formed is converted into the 1,3-dithiole-2-thione by elimination of ethanol with 4-toluenesulfonic acid [120]. In analogous manner the 1,2-dibromoethyl ethyl ether provides with **21** and following elimination of ethanol under basic conditions with lithium diisopropylamide (LDA) the 4,5-vinylenedithio-1,3-dithiole-2-thione in 48% yield [121].



SCHEME 9

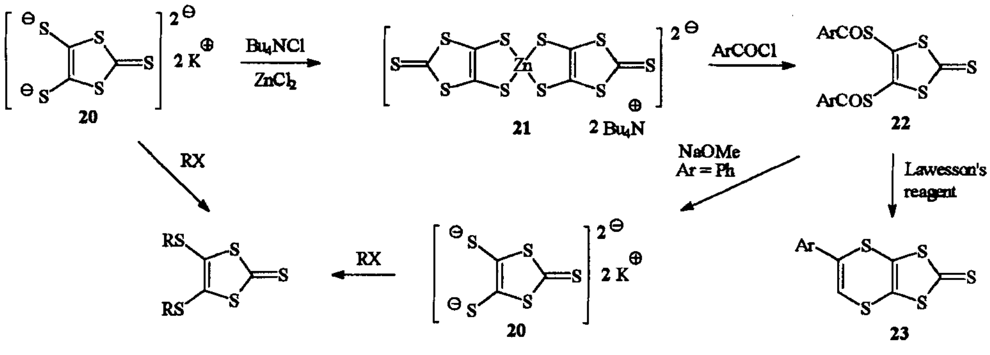
The electrochemical reduction of carbon disulfide on a mercury or platinum electrode in *N,N*-dimethylformamide provides the 4,5-dimercapto-1,3-dithiole-2-thione dianion **20**, which with alkylating agents can form 4,5-bis(alkylthio)-1,3-dithiole-2-thiones [122–124]. On a preparative scale it is better to reduce carbon disulfide with chemical reducing agents. Reduction with sodium [125,126] or potassium [88] in *N,N*-dimethylformamide gives the highest yields.



SCHEME 10

In the electrochemical as well as in the chemical reduction appreciable amounts of trithiocarbonate **18** are formed. The 4,5-dimercapto-1,3-dithiole-2-thione dianion **20** can be separated from the trithiocarbonate **18** as the tetrabutylammonium zinc chelate **21** [127,128]. Compound **21** is converted into 4,5-bis(benzoylthio)-1,3-dithiole-2-thione **22** (Ar = Ph) [125] then to 4,5-dimercapto-1,3-dithiole-2-thione dianion **20** by cleavage with sodium methoxide and afterwards by alkylation to 4,5-bis(alkylthio)-1,3-dithiole-2-thiones [129]. After the reduction the reaction mixture can be alkylated directly, too, so that a separation of **20** from **18** is unnecessary [88,130].

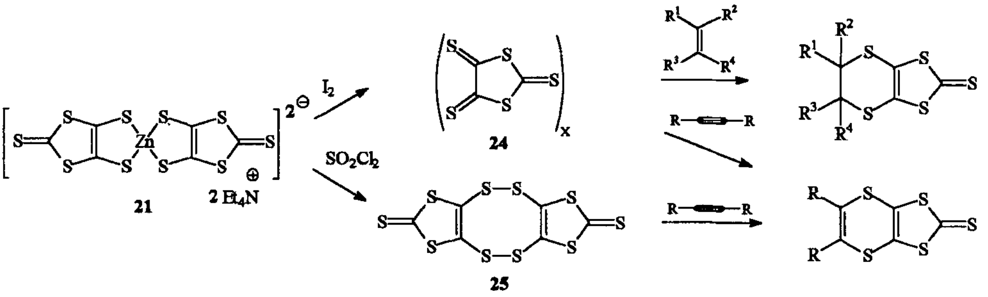
Treatment of **22** with Lawesson's reagent in refluxing toluene affords 1,4-dithiin-fused 1,3-dithiole-2-thiones (Ar = Ph, 4-NO_2Ph) **23** or a thieno-fused 1,3-dithiole-2-thione (Ar = 4-MeOPh) [131].



SCHEME 11

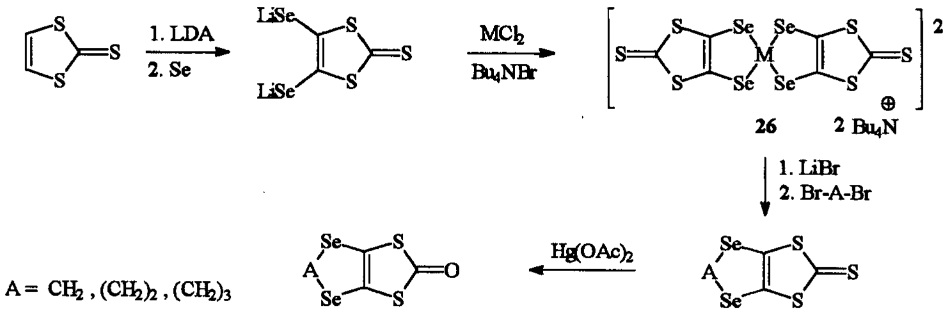
Incorporation of chalcogen atoms into the TTF skeleton involves lithiation of TTF followed by reaction with elemental chalcogen. Then the chalcogenide anion can be capped with dihaloalkanes according to several methods (see also Section 7.1).

Oxidation of bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato) zincate(II) **21** [128] with iodine [132] produces an oligomeric 1,3-dithiole-2,4,5-trithione **24**, which presumably depolymerizes on heating and can be added as well to olefins as to alkynes and provides substituted 1,3-dithiole-2-thiones [130,132–147]. A 1,2,5,6-tetrathiacyclooctadiene **25**, which is formed by the reaction of **21** with sulfuryl chloride reacts with alkynes in the same way [148].



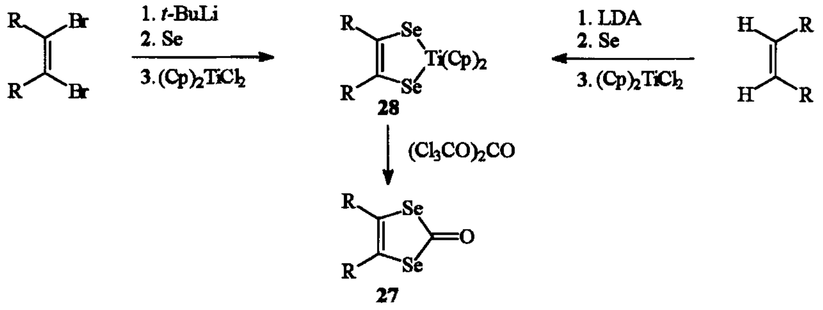
SCHEME 12

An alternative synthesis of selenium substituted TTF starts from the air and moisture stable organometallic complexes bis(tetrabutylammonium) bis(2-thioxo-1,3-dithiole-4,5-diselenolato)nickelate(II) **26** (M = Ni) [149–151] or bis(tetrabutylammonium) bis(2-thioxo-1,3-dithiole-4,5-diselenolato)zincate(II) **26** (M = Zn) [152–155]. These complexes are formed by lithiation of 1,3-dithiole-2-thione, followed by treatment with powdered selenium, nickel chloride or zinc chloride, respectively, and tetrabutylammonium bromide. Upon reflux of the nickel complex **26** with lithium bromide and dibromoalkanes or zinc complex **26** with dibromoalkanes the corresponding (alkylenediseleno)-1,3-dithiole-2-thiones are formed, which can be converted into the (alkylenediseleno)-1,3-dithiol-2-ones with mercury(II) acetate in a refluxing mixture of chloroform and acetic acid.



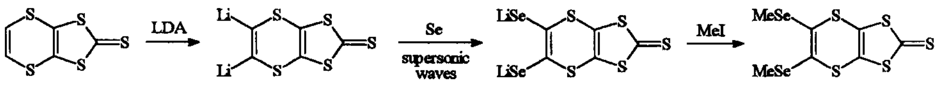
SCHEME 13

1,3-Diselenol-2-ones **27** (obviating the use of highly toxic CSe_2 or H_2Se) are also formed by lithiation of 1,2-dibromoalkanes with *t*-butyllithium or substituted alkenes with LDA, followed by treatment with Se powder. To the reaction mixture titanocene dichloride is added at −78°C. The titanocene complex **28** provides, upon treatment with triphosgene, the corresponding 1,3-diselenol-2-one [156].



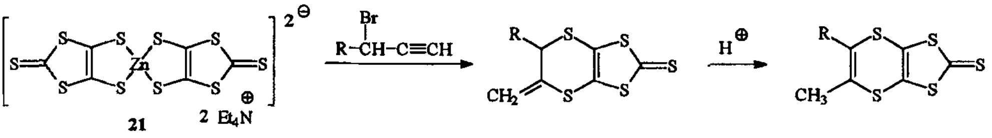
SCHEME 14

Also (vinylenedithio)-1,3-dithiole-2-thione has been lithiated with LDA and substituted, the selenium insertion being facilitated by supersonic waves [157].



SCHEME 15

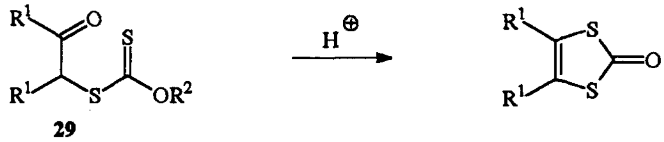
Dialkyl substituted (vinylenedithio)-1,3-dithiole-2-thiones have been prepared by reflux of the complex bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato) zincate(II) **21** with propargyl halides in acetone and subsequent isomerization with 4-toluenesulfonic acid [158].



SCHEME 16

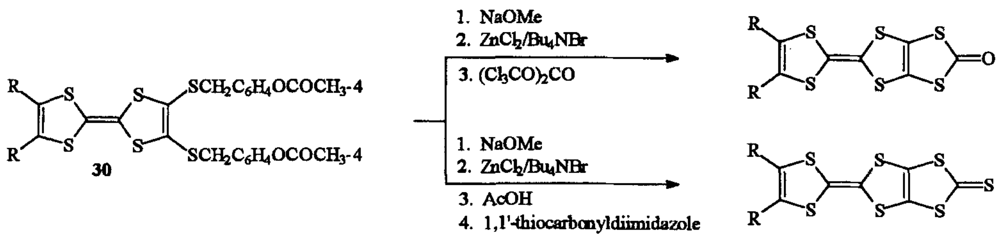
This reaction is assumed to be analogous to the formation of dimethylenetetrahydro-TTF **86** by cleavage of 4,5-bis(propargylthio)-1,3-dithiol-2-ones in alkaline solution (see Section 1.11) [159].

1,3-Dithiol-2-ones can be prepared directly by cyclization of *β*-keto *O*-alkyl dithiocarbonates with acids. 4,5-(Ethylenedithio)-1,3-dithiol-2-one has been synthesized in 50% yield by treatment of 2-oxo-3-(*i*-propoxythiocarbonylthio)-1,4-dithiane **29** ($R^1 = S(CH_2)_2S$, $R^2 = i\text{-}C_3H_7$) with sulfuric acid at 0°C [160,161], 4-bromophenyl-1,3-dithiol-2-one in 24% yield by reaction with perchloric acid in ether/dichloromethane (1 : 1) [162], and bis-4,5-(2- or 3-thienyl)-1,3-dithiol-2-ones by reaction of the corresponding *β*-keto *O*-ethyl dithiocarbonate **29** with a solution of HBr in acetic acid [163,164].



SCHEME 17

A method for the synthesis of fused 1,3-dithiol-2-ones has been developed in the shape of reaction of **30** with excess of sodium methoxide in dichloromethane/methanol at room temperature, subsequent treatment with zinc chloride and tetra-*n*-butylammonium bromide, followed by excess of triphosgene in THF at −78°C [165,166]. The corresponding TTF fused 1,3-dithiole-2-thione is synthesized if the formed zinc-dithiolato complex is converted with acetic acid to the tetrathiafulvalene-4,5-dithiol and was subsequently allowed to react with 1,1′-thiocarbonyldiimidazole [167,168].

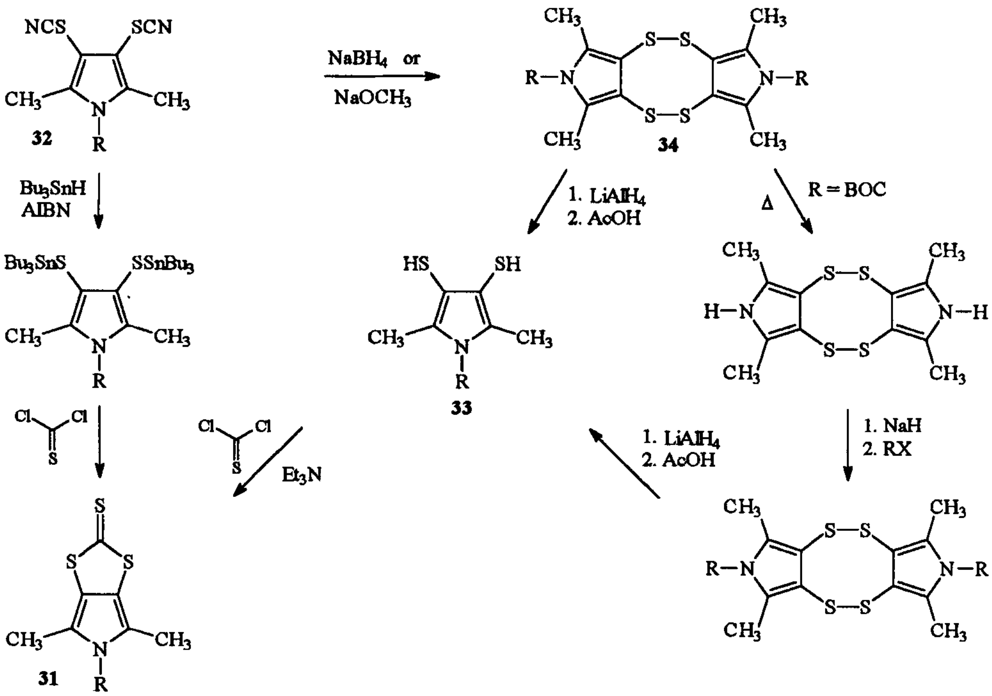


SCHEME 18

Thermolysis of 1,2,3-thiadiazole **8** under pressure at 220°C in carbon disulfide allows the synthesis of trimethylene- and tetramethylene-1,3-dithiole-2-thione in moderate yields (41 and 43%, respectively) and of benzo-1,3-dithiole-2-thione in good yield (84%) [169,170]. In the presence of sodium hydride in acetonitrile the reaction proceeds at room temperature or under reflux affording 4-substituted 1,3-dithiole-2-thiones [171].

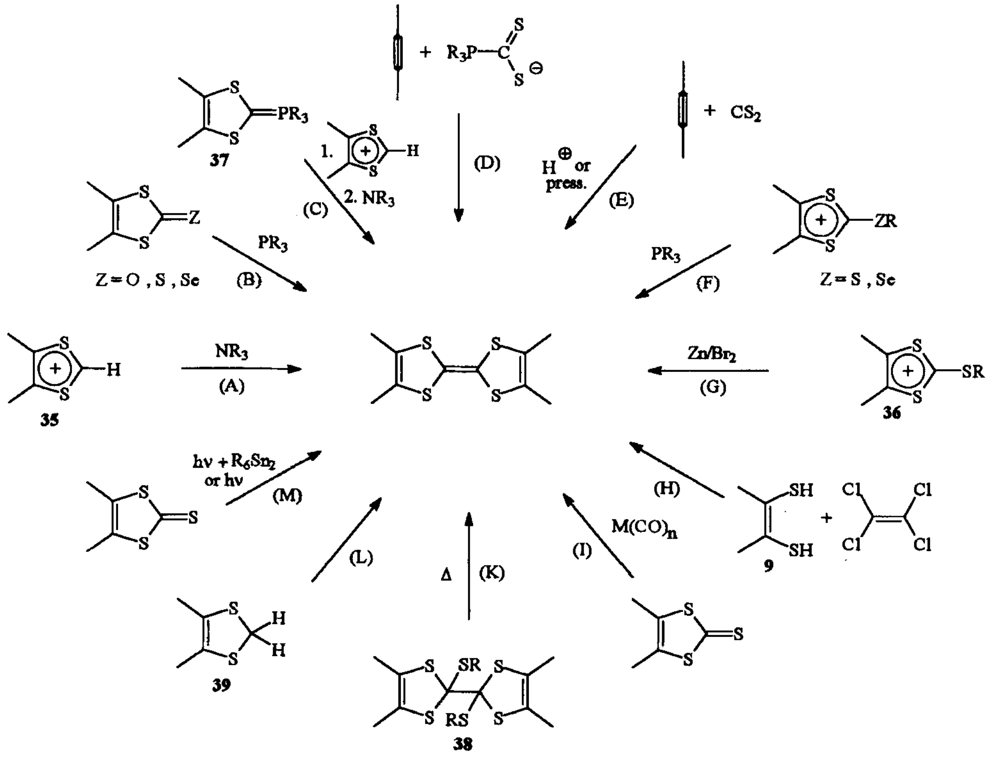
Benzo-annelated and heterocyclo substituted 1,3-dithiole-2-thiones have been formed by treatment of the 1,2-dimercapto compounds **9** with carbon disulfide in alkaline solution or with thiocarbonyldiimidazole in glacial acetic acid/tetrahydrofuran (Scheme 1) [172–176].

Pyrrolo-substituted 1,3-dithiole-2-thiones **31** have been synthesized by using of 3,4-dithiocyanopyrroles **32** as starting materials. The radical-initiated reaction of **32** with tributyltin hydride provides the corresponding bis(tributylstannyl) compound [177], which is converted with thiophosgene into the heterocyclo substituted 1,3-dithiole-2-thione **31**. Simpler is the reduction of **32** with lithium aluminium hydride to the air-sensitive dithiole **33** and subsequent reaction with thiophosgene in the presence of triethylamine. The third way to prepare **31** is the best one and includes the conversion of the thiocyanate **32** to a disulfide **34** by a nucleophile (sodium borohydride, sodium methoxide or hydrazine, respectively). Reduction of **34** with lithium aluminium hydride affords the dithiole **33**, which is reacted with thiophosgene to give **31** in high yields. In the case of R = *t*-butoxycarbonyl (BOC) this protecting group in **34** is removed by heating to 180°C, resulting in the unsubstituted **34**. The formation of the unsubstituted **34** opens the possibility to prepare a variety of substituted **34** by reaction with sodium hydroxide in DMF and following alkylation with alkyl halides, which can be further converted to **31** [178].



SCHEME 19

The 1,3-dithiole-2-thiones can be converted into TTF in different ways. The most important methods are summarized in Scheme 20.



SCHEME 20

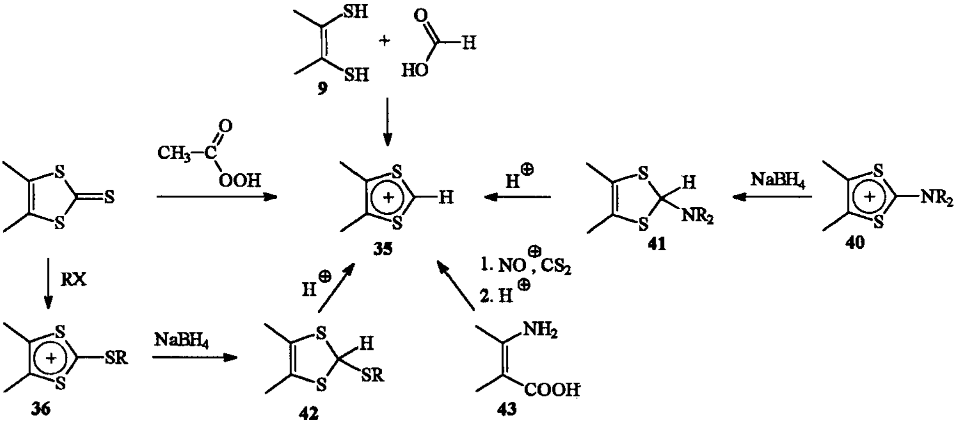
1.2. TTF by Deprotonation of 1,3-Dithiolium Salts (Method A)

Treatment of 2*H*-1,3-dithiolium salts **35** with tertiary aliphatic amines (*N*-ethyldiisopropylamine, triethylamine) in acetonitrile or acetone provides TTF in large quantities. 1,3-Dithiolium salts are stable compounds because the 1,3-dithiolium cation is resonance stabilized. They can be prepared in different ways (Scheme 21) [179–183].

1,3-Dithiolium salts **35** 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 [84,96]. 1,3-Dithiole-2-thiones with acceptor substituents in the 4- and 5-position cannot be converted into 1,3-dithiolium salts **35** in this way [184]. TTF with electron-withdrawing substituents are formed in high yields by method B.

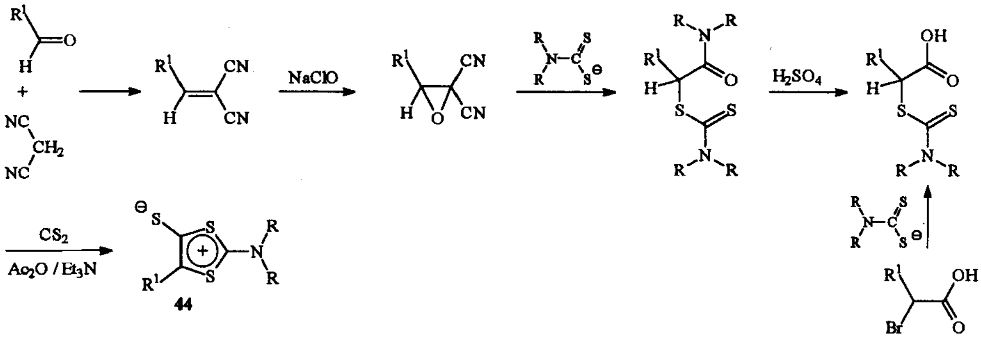
2-(*N*,*N*-Dialkylamino)- **40** and 2-(alkylthio)-1,3-dithiolium salts **36** are converted into 1,3-dithiolium salts **35** by reduction with sodium borohydride, followed by treatment with acid [83,185,186]. Benzo- or naphtho-annelated 1,3-dithiolium salts **35** are obtained by the reaction of the 1,2-dimercapto compounds **9** with formic acid [187–190] or by that of *β*-amino carboxylic acids **43** with isopentyl nitrite in 1,2-dichloroethane in the presence of carbon disulfide and treatment of the thus obtained

2-isopentyl-1,3-dithiole with acid [191]. Naphtho-annelated or heterocyclo substituted 1,3-dithiolium salts **35** 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 **36** with sodium borohydride and reaction of the 2-(alkylthio)-1,3-dithioles **42** with acid [173,178,192].



SCHEME 21

Intermediates for 2*H*-1,3-dithiolium salts are also the mesoionic 1,3-dithioles **44** which can be obtained in a multi-step reaction [193,194]. An improved synthesis of **44** involves reaction of a 2-halo carboxylic acid with excess of *N*,*N*-dialkyldithio-carbamate in ethanol. The crude product is treated (without further purification) with acetic acid anhydride and triethylamine, followed by reaction with excess of carbon disulfide [195]. After alkylation of **44** the 1,3-dithiolium salts **35** can be obtained via the known route, i.e. by reduction with sodium borohydride and subsequent deamination with strong acid (Scheme 21).



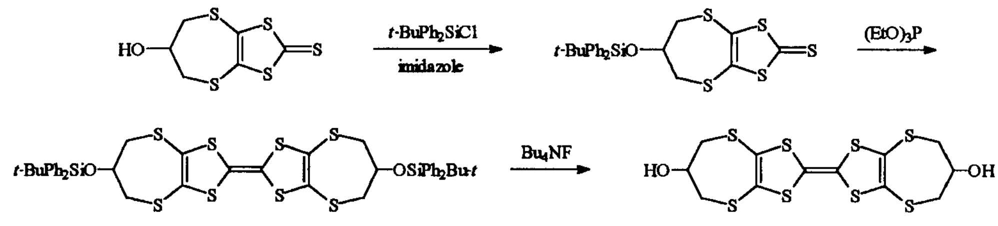
SCHEME 22

1,3-Dithiolium salts **35** 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 of their high solubility and hygroscopic properties hydrogen sulfates are inconvenient.

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

After the conversion of 1,3-dithiolane-2-thiones with phosphites to tetrathioethenes [196], the formation of TTF by desulfurization of 1,3-dithiole-2-thiones with trivalent phosphorus compounds was also successful [197]. 1,3-Dithiole-2-thiones undergo the desulfurization reaction only when they are substituted by electron-withdrawing groups (COOR, CF_3, CN) [197–200], by alkylthio groups [99,201–203], by heterocycles [173,202], or if they are benzo-annelated [189,204].

Some functional groups in 1,3-dithiole derivatives do not survive the reaction conditions in the coupling of 1,3-dithiole derivatives (e.g. hydroxy, keto or aldehyde groups) and provide no TTF derivatives or only low yields. Better yields were obtained after protection of the formyl group as acetal [171,205,206], the keto group as ketal [207] or the hydroxyalkyl group as *t*-butyldiphenylsilyl ether [145,208–213], methoxyethoxymethoxy ether [214–216], tetrahydropyranoether [114,217,218], or ester [219,220]. After coupling, for example, the *t*-butyldiphenylsilyl protecting group is removed with fluoride ions.

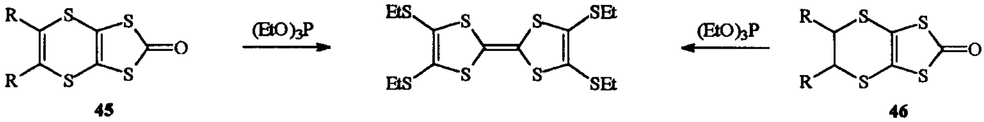


SCHEME 23

As trivalent phosphorus compounds, trialkyl or triaryl phosphites as well as triphenylphosphine are convenient [198,200]. Often the yields of TTF are higher with 1,3-dithiol-2-ones or -selones than with 1,3-dithiole-2-thiones [99,173,178,198,202,221].

1,3-Dithiole-2-thiones can be easily converted into 1,3-dithiol-2-ones by reaction with mercury(II) acetate in chloroform–glacial acetic acid [222] or into 1,3-dithiole-2-selones after alkylation and subsequent treatment with hydrogen selenide [223].

Different from the formation of TTF provide the tetrathiaindenone **45** ($R = COOCH_3$) or the dihydrotetrathiaindenone **46** ($R = Ph$) with neat triethyl phosphite the tetraethylthio-TTF [140,142,148].



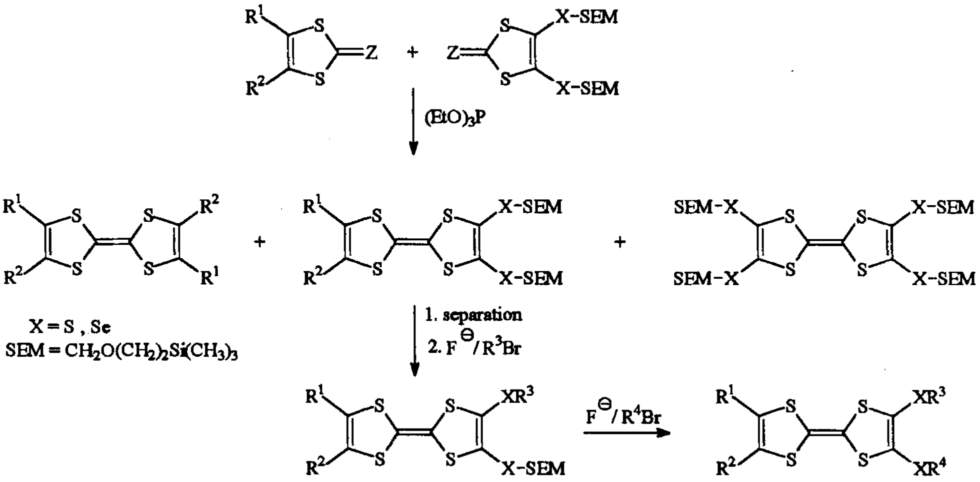
45 **46**

SCHEME 24

Cross-coupling of the appropriate 1,3-dithiole derivatives with triethyl phosphite usually leads to a mixture of the three possible TTF. The difficulty of their separation can be overcome by use of trimethylsilylethoxymethyl (SEM) as a protecting group for the 1,3-dithiole derivatives. The three protected compounds thus formed can be easily separated by column chromatography. In a subsequent reaction the protecting group is removed under mild conditions with tetrabutylammonium fluoride and the free anion alkylated with an alkyl bromide [224]. Higher yields of unsymmetrical TTF are attained by cross-coupling of 1,3-dithiole derivatives by carrying out the reaction stepwise [225].

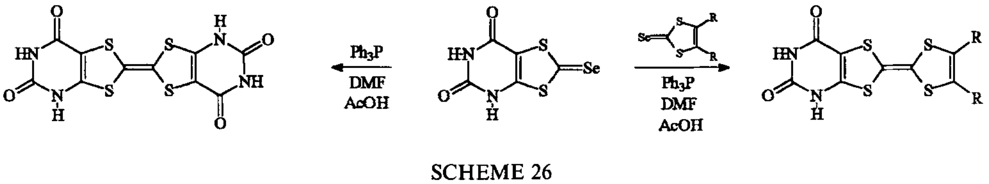
The yield of alkylthio substituted TTF by coupling of 1,3-dithiole-2-thiones with trimethyl or triethyl phosphite is increased by high pressure (4–8 kbar) [226].

Complications can arise from a ring opening attack of the fluoride ion to the protons of 1,2-dithioethylene bridge and formation of a mercapto anion which can be alkylated (see also Section 7.1) [224,227].



SCHEME 25

Pyrimido substituted TTF are formed by coupling of the appropriate dithiole-2-selones with triphenylphosphine in *N*,*N*-dimethylformamide in the presence of acetic acid at room temperature. The selones do not react with triethyl phosphite in benzene at 80°C [228].

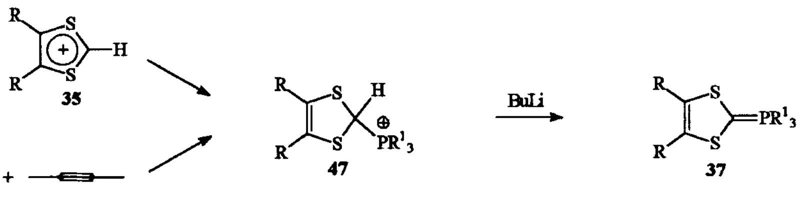


SCHEME 26

1.4. Treatment of 1,3-Dithiolium Salts with Phosphoranes or Phosphonates (Method C)

1,3-Dithiol-2-ylidenephosphoranes **37** are prepared, as unstable compounds, by deprotonation of 1,3-dithiolylphosphonium salts **47** with butyllithium at −78°C in tetrahydrofuran [229–234]. 1,3-Dithiolylphosphonium salts **47** are obtained in the case of alkyl substituted, unsubstituted, and benzo-annelated compounds by reaction of the

1,3-dithiolium salts **35** with a phosphine. Because 1,3-dithiolium salts **35** with electron-withdrawing substituents in the 4- and 5-position can only be formed with difficulty, these 1,3-dithiolylphosphonium salts **47** are better synthesized by treatment of alkynes with an adduct of carbon disulfide and a phosphine in acidic solution at – 65°C in ether [232,233,235].

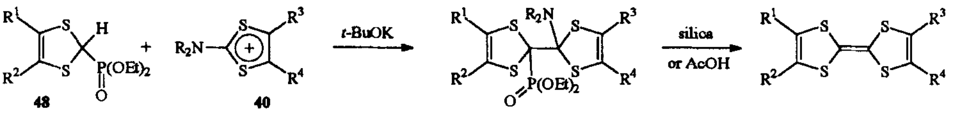


SCHEME 27

The thus prepared 1,3-dithiol-2-ylidenephosphoranes **37** react in the presence of triethylamine with 1,3-dithiolium salts **35** to form TTF [230,232,236]. This method has the great advantage that unsymmetrical TTF derivatives can be prepared. The instability of the 1,3-dithiol-2-ylidenephosphoranes **37** under the reaction conditions leads to the formation of variable amounts of symmetrical TTF. Therefore, purification of the mixture by column chromatography is necessary [237]. Other methods for the synthesis of unsymmetrical TTF by coupling of two different 1,3-dithiole derivatives require separation from symmetrical co-products by fractional recrystallization [172,238,239] or chromatography [240,241].

This side reaction and the formation of symmetrical TTF can be avoided by coupling of phosphonate esters of various substituted 1,3-dithioles **48** with 2-amino-1,3-dithiolium salts **40** under Wittig-like conditions. Yields of pure, unsymmetrical TTF are typically 30–50% [195,242–244]. Mechanistic investigations show that the yield of the TTF derivative is dependent on the ratio of the concentration of acetic acid and the formed intermediate [245,246].

The reaction between disubstituted phosphonates (substituted by alkyl or heteroatomic groups or benzosubstituted) and unsubstituted or mono- or disubstituted iminium salts (substituted by alkyl or heteroatomic groups) is successful. Piperidino-substituted iminium salts furnish better yields than dimethylamino-substituted iminium salts [247]. Mono- or unsubstituted phosphonates form only with reactive iminium salts the corresponding TTF in moderate yields (30%) [248].

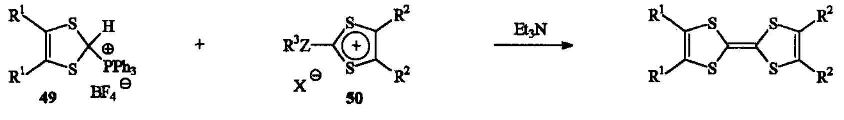


SCHEME 28

The required phosphonate esters of 1,3-dithioles **48** are synthesized by a Michaelis–Arbuzov reaction of 1,3-dithiolium salts **35** with trialkylphosphites in the presence of an equimolar amount of sodium iodide in dry acetonitrile under nitrogen at room temperature [229,231]. Some substituted **48** can be also prepared in a one-step reaction by heating of the corresponding 1,3-dithiole-2-thiones or -2-ones in the presence of a trialkyl phosphite at high dilution [243,249–251], or in neat trialkyl phosphite

[178,252]. Using deuterated triethyl phosphites [$P(OCH_2CD_3)_3$, $P(OCD_2CH_3)_3$] proved that proton transfer occurs from the CH_2 group in the neighbourhood of the oxygen atom [253]. Formation of the phosphonate ester **48** is postulated by initiation not only by oxophilic or thiophilic attack but also by carbophilic attack of phosphorus at the -one or -thione functions [178,252].

Substitution of the 2-amino-1,3-dithiolium salts **40** by 2-alkylthio- or 2-alkylseleno-1,3-dithiolium salts **50** provide with the 1,3-dithiol-2-ylidenephosphoranes **49** the corresponding TTF. This route represents also a clean method of obtaining unsymmetrical TTF derivatives [254–260].

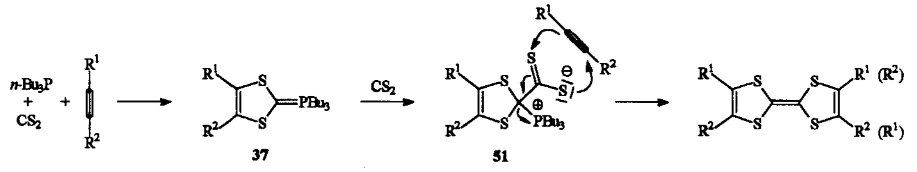


$R^1 = COOCH_3, SCH_3, SC_{16}H_{33}, SCOPh, S(CH_2)_2CN, S(CH_2)_2S$ Z = S, Se
$R^2 = H, CH_3, C_{17}H_{35}, (CH{=}CH)_2, SCH_2COOCH_3, Se(CH_2)_2Se$
$R^3 = CH_3, C_2H_5$

SCHEME 29

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

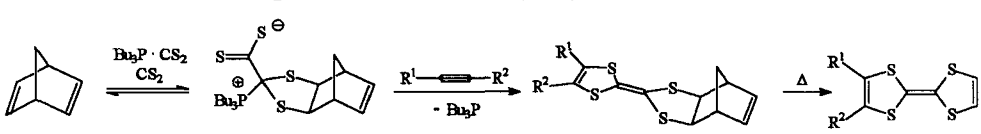
The reaction of the adduct between carbon disulfide and tributylphosphine with an electron-withdrawing substituted alkyne at −30°C in tetrahydrofuran provides the corresponding 1,3-dithiol-2-ylidenephosphorane **37** [261], which gives with an excess of carbon disulfide the zwitterionic intermediate **51** [116]. **51** could further react with the alkyne to the corresponding TTF [261]. Also alkynes with electron-donating substituents form with the adduct 1,3-dithiol-2-ylidenephosphoranes **37** [262].



$R^1 = H, R^2 = COOCH_3$

SCHEME 30

Analogously, the reaction of the adduct between carbon disulfide and tributylphosphine yields with alkenes the corresponding 1,3-dithiolan-2-ylidenephosphoranes, which can be further converted into dihydro-TTF by reaction with carbon disulfide and alkynes [263]. Upon flash vacuum pyrolysis the dihydro-TTF undergoes a retro Diels–Alder reaction to give substituted TTF [264].



$R^1 = COOCH_3, COOC_2H_5$
$R^2 = H, C_6H_5, COOCH_3, COOC_2H_5$

SCHEME 31

Electron-deficient alkynes form with carbon disulfide, activated by iron complex **52** [265,266] or nickel complex **53** [267], TTF in moderate yields (25–30%, or 50%, respectively). In the case of the nickel complex **53** the yield is increased in the presence of carbon monoxide (62%). The formation of TTF derivatives from complexes of electron-deficient alkynes and iron complexes **52** can be initiated either by electrochemical or by chemical oxidation with $AgCF_3SO_3$, I_2, or $[Fe(C_5H_5)_2]PF_6$ [119,268,269].

$L = Ph_3P, (MeO)_3P$

triphos = $CH_3C(CH_2PPh_2)_3$

52 **53**

SCHEME 32

Alkynes with electron-withdrawing substituents and carbon disulfide react at 100°C in a sealed tube to form TTF derivatives in very low yield (2%) [197]. The preparation of TTF in high yield is achieved by carrying out the reaction under high pressure (5–6 kbar) [270–272], or in the presence of strong acids (trifluoroacetic acid) [197,273]. Cycloalkynes provide with carbon disulfide at room temperature the corresponding TTF [274–277] and thiacycloalkynes at 100°C in a sealed tube [278].

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 triphenyl-phosphine 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 hexamethylphosphoramide can be used as the trivalent phosphorus compound [279,280].

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 treatment of 2-(methylthio)-1,3-dithiolium salts **36** (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, protic acids, methyl iodide, or dimethyl sulfate. The yield reaches values between 35 and 65% [281–283].

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

By treating 1,2-dimercaptobenzene derivatives **9** with tetrachloroethene under basic conditions (*N*,*N*-diisopropylethylamine, triethylamine, pyridine, *N*,*N*-dimethylformamide) one can obtain TTF in modest yields (5–35%) [172,284]. This method was used in 1926 for the synthesis of the first tetrathiafulvalene [285]. In the case of a 3,4-dimercaptopyrrole only a dichlorofulvene intermediate was formed [178].

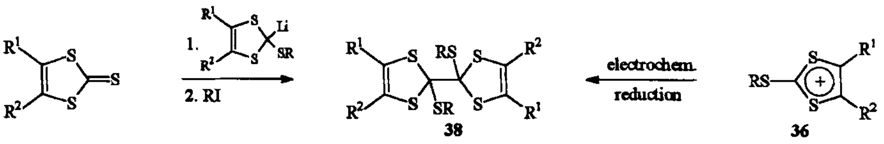
1.9. Miscellaneous Methods

A photochemical method for the synthesis of TTF is the irradiation of 1,3-dithiole-2-thiones with UV light in benzene. The yields are modest (5–25%), better in the presence of triethylamine or triethyl phosphite. 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 [286–288].

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 applicable for the preparation of TTF substituted either by electron-donating or electron-withdrawing groups (method M, Scheme 20) [178,289–291].

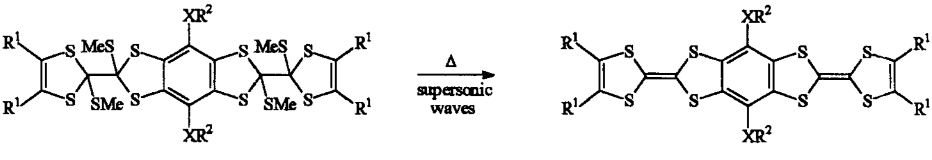
In a one-step synthesis TTF are afforded directly from 1,3-dithiole-2-thiones, substituted with electron-donating or electron-withdrawing groups, in 10–60% yield by heating with dicobaltoctacarbonyl or triirondodecacarbonyl in benzene or toluene solutions (method I, Scheme 20) [118,198,292]. Cross-coupling of two different substituted 1,3-dithiole-2-thiones provides the unsymmetrical substituted TTF after separation from symmetrical substituted TTF [293].

Thermolysis of the orthothiooxalates **38** in carbon tetrachloride gives TTF in high yield [123,294]. The addition of catalytic amounts of 4-toluenesulfonic acid accelerates the reaction [294]. The orthothiooxalates **38** are formed by electrochemical reduction of the 2-(alkylthio)-1,3-dithiolium salts **36** [123,295,296] or by treatment of 1,3-dithiole-2-thiones with 2-lithio-2-(alkylthio)-1,3-dithioles and alkylation of the intermediates formed [260,297]. 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. This last method for the synthesis of orthothiooxalates **38** allows the formation of unsymmetrical TTF in their pure form (method K, Scheme 20).



SCHEME 33

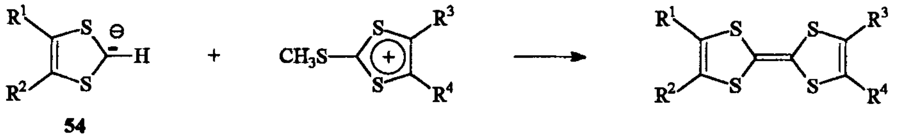
Addition of catalytic amounts of 4-toluenesulfonic acid does not influence the thermolysis of bis(orthothiooxalates) in 1,1,2,2-tetrachloroethane at 130°C [298,299]. However, upon supersonic irradiation the reaction proceeds at lower temperatures (70°C) in a yield as high as 80% [300–303].



R^1 = SBu, SHex, S$(CH_2)_2$S, $(CH{=}CH)_2$ X = O, S
R^2 = Me, Et, *i*-Am, Hex, Dodec

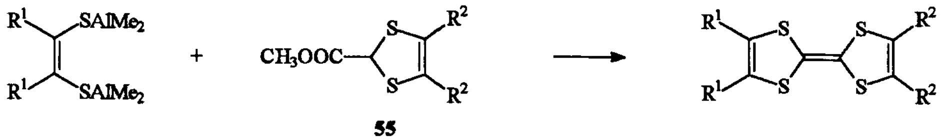
SCHEME 34

A coupling method leading to unsymmetrical TTF involves treatment of 1,3-dithiole anions **54** with electrophilic 1,3-dithiolium salts. In addition to the expected condensation products, symmetrical TTF, derived from **54**, probably via carbenes, are formed [304].



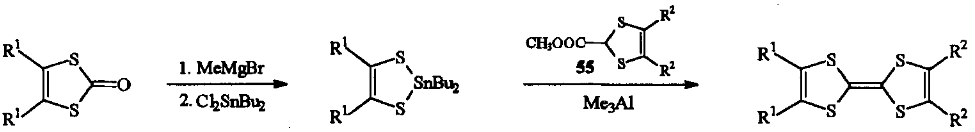
SCHEME 35

The reaction of organoaluminium reagents with the ester of the 1,3-dithiole **55** gives also the possibility of the synthesis of unsymmetrical substituted TTF [305]. Similarly the bis(dimethylaluminium)-1,2-benzenedithiole reacts with 1,3-benzoxathiole-2-carboxylic methyl ester and provides the dibenzooxatrithiafulvalene [306].



SCHEME 36

In an analogous manner tin thiolates, formed by reaction of the corresponding 1,3-dithiol-2-ones with methylmagnesium bromide (3.3. equiv) in THF and subsequent trapping by dichlorodibutyltin [307], provide also unsymmetrical TTF with the ester of the 1,3-dithiole **55** in the presence of trimethylaluminium [308–313].



SCHEME 37

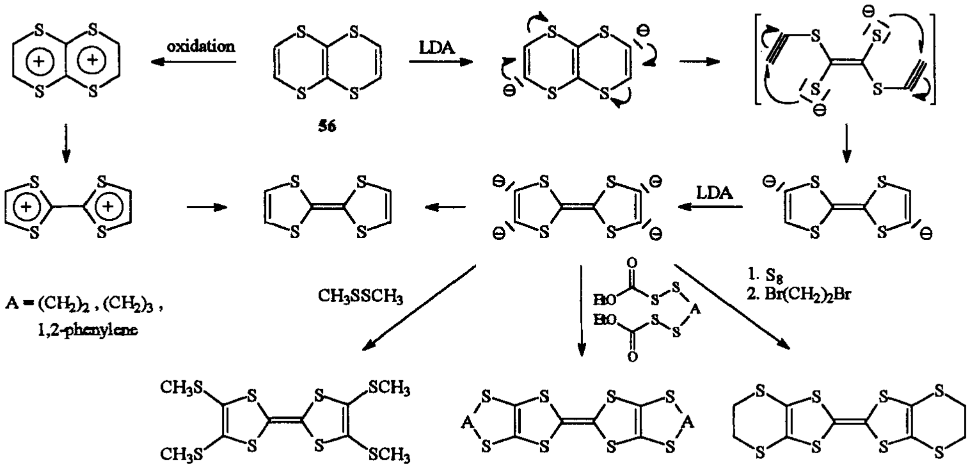
Thermolysis of 2-alkoxy-1,3-dithioles also produces TTF [314]. The yield increases if the thermolysis is performed in benzene in the presence of trichloroacetic acid [194,315,316].

Electrochemical oxidation of 1,3-dithioles **39** in acetonitrile, in the presence of pyridine, provides TTF directly (method L, Scheme 20) [317].

1,4,5,8-Tetrathiatetraline **56** is rearranged intramolecularly under strong basic conditions (LDA in THF) and yields tetrathiafulvalene (70%). The formation of acetylenic bonds and recyclization is proposed. In diethyl ether the rearrangement does not occur [318]. In the presence of additional disulfides [318], bisdisulfides, [319] or sulfur and alkylhalides [320,321] the corresponding TTF derivatives are synthesized. In a large scale synthesis the rearrangement of **56** to tetrathiafulvalene was achieved with potassium *t*-butoxide [322].

Electrochemical oxidation of the 1,4,5,8-tetrathiatetraline to the dicationic state leads to rearrangement of the dication and formation of the TTF-dication. The same process is observed by oxidation with lead tetraacetate in trifluoroacetic acid at 0°C. Subsequent reduction with sodium dithionite yields tetrathiafulvalene (54%). If the electrochemical oxidation occurs to the radical cation, no rearrangement is observed [323].

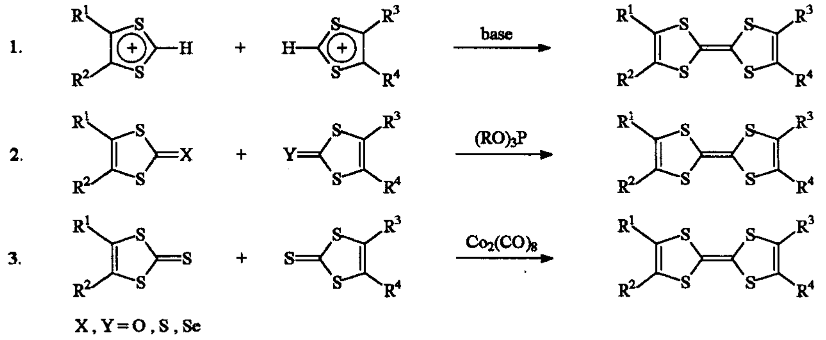
In the case of the 1,4,5,8-tetratelluratetraline the rearrangement by electrochemical oxidation is not observed [324]. A similar skeletal rearrangement is also reported for the electrogenerated dication of 1,4,5,8-tetrathiaoctaline [325,326].



SCHEME 38

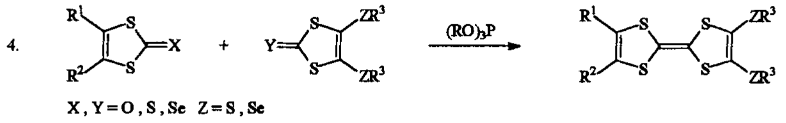
1.10. Formation of Unsymmetrical Substituted TTF

For preparing unsymmetrical substituted TTF the same methods used for synthesizing symmetrically substituted TTF can be used. Cross-coupling of two different substituted 1,3-dithiole derivatives provides a mixture of the three possible TTF, which are separated by fractional crystallization or column chromatography (method 1 [238,239,327], method 2 [208,240,254,328–331], method 3 [329]).



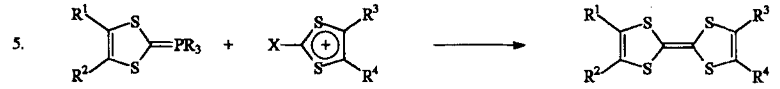
SCHEME 39

In the case of thio- or seleno-substituted 1,3-dithiole compounds cross-coupling of protected 1,3-dithiole derivatives gives better results. The properties of the three formed TTF show greater distinctions than the unprotected and permit an easier separation by column chromatography. The protecting groups ($R^3 = CH_2CH_2CN$ [255,332–334], $R^3 = CH_2C_6H_4OCOCH_3$-4 [335–337], $R^3 = CH_2OCH_2CH_2Si(CH_3)_3$ [224]) are generally removed under mild conditions.



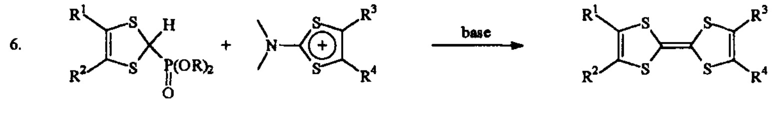
SCHEME 40

1,3-Dithiol-2-ylidenephosphoranes, prepared by deprotonation of 1,3-dithiolylphosphonium salts, provide with 1,3-dithiolium salts the unsymmetrical substituted TTF (X = H [230,232,236,255,338], X = SR [255], X = SeR [254,256,257,259]).



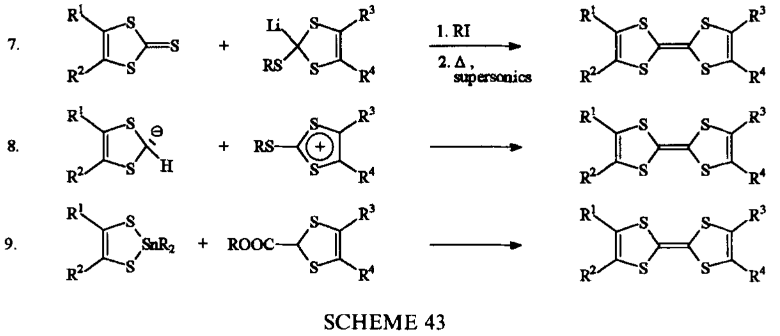
SCHEME 41

In method 5 the formation of variable amounts of symmetrically substituted TTF is observed. This side reaction can be avoided by coupling of the phosphonate ester of 1,3-dithiolium derivatives with 2-amino-1,3-dithiolium salts in the presence of a strong base [195,242–244,327,339–343].



SCHEME 42

Furthermore, some special couplings of 1,3-dithiole derivatives yield unsymmetrically substituted TTF (method 7 [297,344,345], method 8 [304], method 9 [305,307,308,310]).

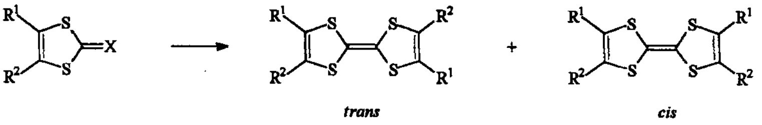


SCHEME 43

TTF and their data are summarized in Table A1.

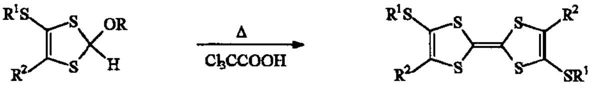
1.11. Formation of *cis*- and *trans*-Isomers of TTF

Coupling of unsymmetrically substituted 1,3-dithiole derivatives by various methods normally provides TTF as a mixture of *cis*- and *trans*-isomers.



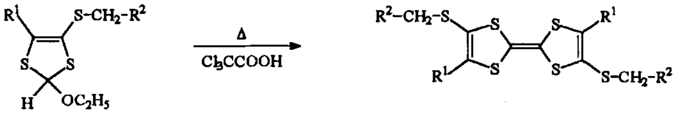
SCHEME 44

Only in the case of thermolysis of 2-alkoxy-1,3-dithioles in the presence of trichloroacetic acid in refluxing benzene could the formation of *trans*-isomers be demonstrated by X-ray analysis [346].



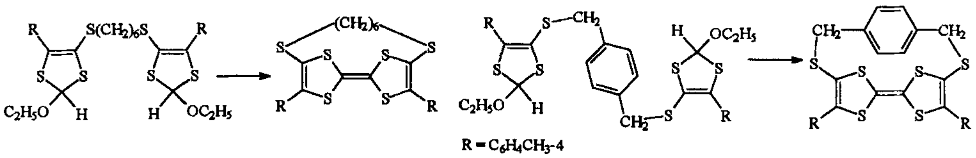
SCHEME 45

By thermolysis of 2-alkoxy-1,3-dithioles in the presence of trichloroacetic acid *trans*-TTF with covalently bonded acceptors on the donor unit can be prepared [316].



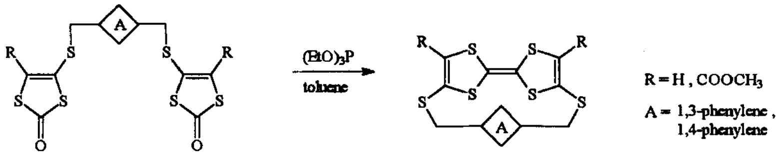
SCHEME 46

In two cases, however, bridged 2-alkoxy-1,3-dithioles form the *cis*-isomers in nearly quantitative yield [347].



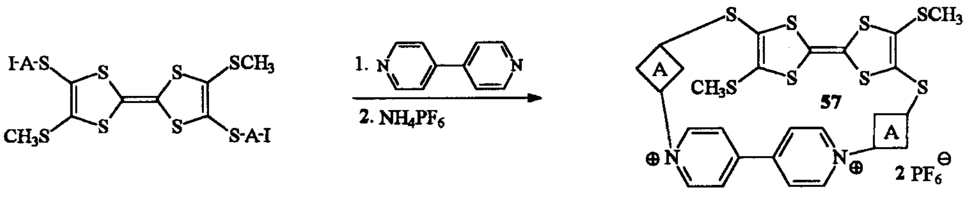
SCHEME 47

Cis-isomers are also obtained by refluxing of bis-1,3-dithiol-2-ones with triethyl phosphite in toluene. In an intramolecular reaction the 1,3- and 1,4-derivatives are formed. Attempts to prepare the 1,2-derivative failed [348].



SCHEME 48

In **57** with A = $(CH_2)_4$ the *trans*-isomer has a rigid structure and only this isomer is isolated, established by X-ray structure analysis. In the case of A = $(CH_2)_5$ or R = $(CH_2)_2O(CH_2)_2$ a *cis*/*trans* mixture is formed [349].



SCHEME 49

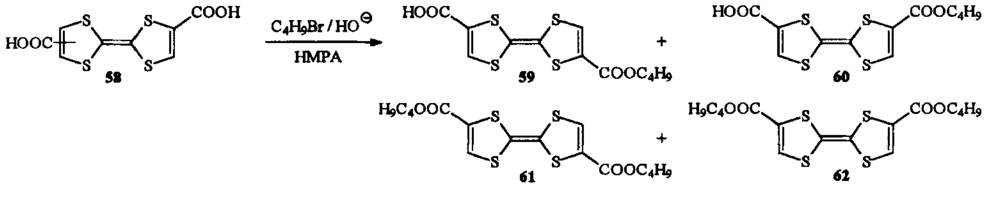
Mostly the properties of *cis*- and *trans*-isomers of TTF are very similar and prevent a distinction or separation. Sometimes the *trans–cis* isomerization can be forced by various methods.

1.11.1. Acid Catalysed

In a ^{1}H NMR study for the first time evidence of an acid catalysed *trans–cis* isomerization was obtained in the case of 5,4′-di(4-chlorphenyl)-4,5′-di(methylthio)tetrathiafulvalene [350]. The *cis–trans* equilibrium was too rapidly established to permit isolation of the pure *cis* form. Only the *trans*-isomer could be recovered after concentration of the solution.

1.11.2. Light Induced

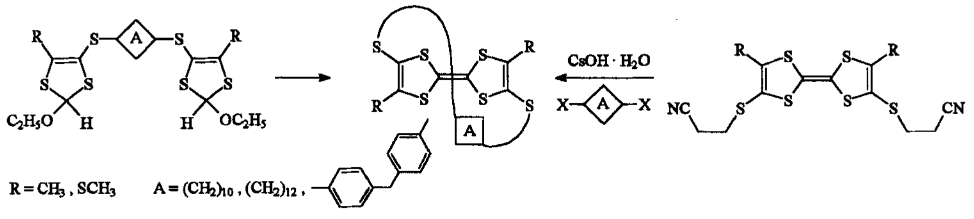
Esterification of tetrathiafulvalenedicarboxylic diacid **58** with *n*-butyl bromide in hexamethylphosphoramide (HMPA) at room temperature provides a mixture of two monoesters **59**, **60** and two diesters **61**, **62**. Also by their different solubility in acetonitrile, benzene and hexane the *cis*- and the *trans*-isomer as well from the monoester from the diester could be separated. In each case the *cis*- and the *trans*-isomer show few differences in the ^{1}H NMR, UV–Vis, and IR spectra [351]. By irradiation with sunlight the *trans*-diester **61** isomerizes to the *cis*-isomer **62** [352].



SCHEME 50

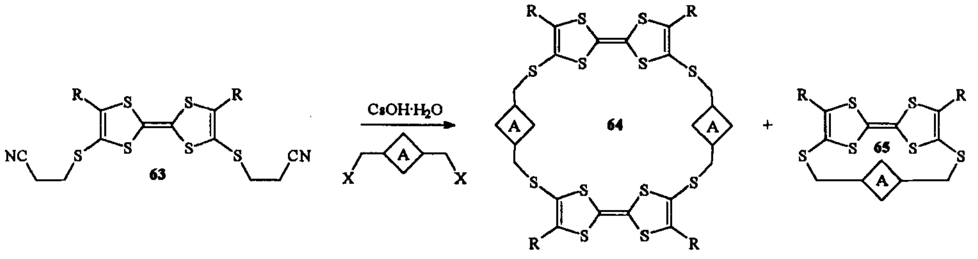
1.11.3. Electrochemical Induced

If the bridge is long enough ($(CH_2)_n$ with $n = 10$ or 12) in bridged TTF the *trans*-isomer is formed. During electrochemical oxidation the *trans*-isomer is converted into the *cis*-isomer [348,353].



SCHEME 51

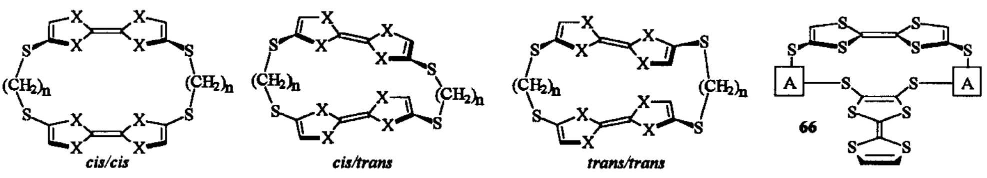
Starting from a *cis*/*trans* mixture of **63** after deprotection with cesium hydroxide and alkylation the tetrathiafulvalenophanes **64** as an inseparable *cis*/*trans* mixture are formed (A = ethynediyl) [354]. By successive deprotection with cesium hydroxide and alkylation the *cis*/*trans* mixture of **64** is also the only product (A = diphenylmethane-4,4′-diyl) [348]. If the bridging group A is long enough (A = 1,3-butadiyne-1,4-diyl, biphenyl-4,4′-diyl), **65** is the main product, where in the case of A = 1,3-butadiyne-1,4-diyl the *cis*-isomer could be separated (after X-ray analysis) and in the case of the longer bridge A = biphenyl-4,4′-diyl the *trans*-isomer [354]. Under high dilution conditions the reaction leads only to the *cis*/*trans* mixture of **65** [348]. But in the case of R = SCH_3 and A = $(CH_2CH_2O)_nCH_2CH_2$ the *trans*-isomer ($n = 3$) or the *cis*-isomer ($n = 4,5$) could be separated by fractional crystallization [355]. A *cis*/*trans* mixture of **65** with pyromellitic diimide as bridging group crystallizes in two different forms representing the *cis*- and *trans*-isomer, which could be separated mechanically [356].



SCHEME 52

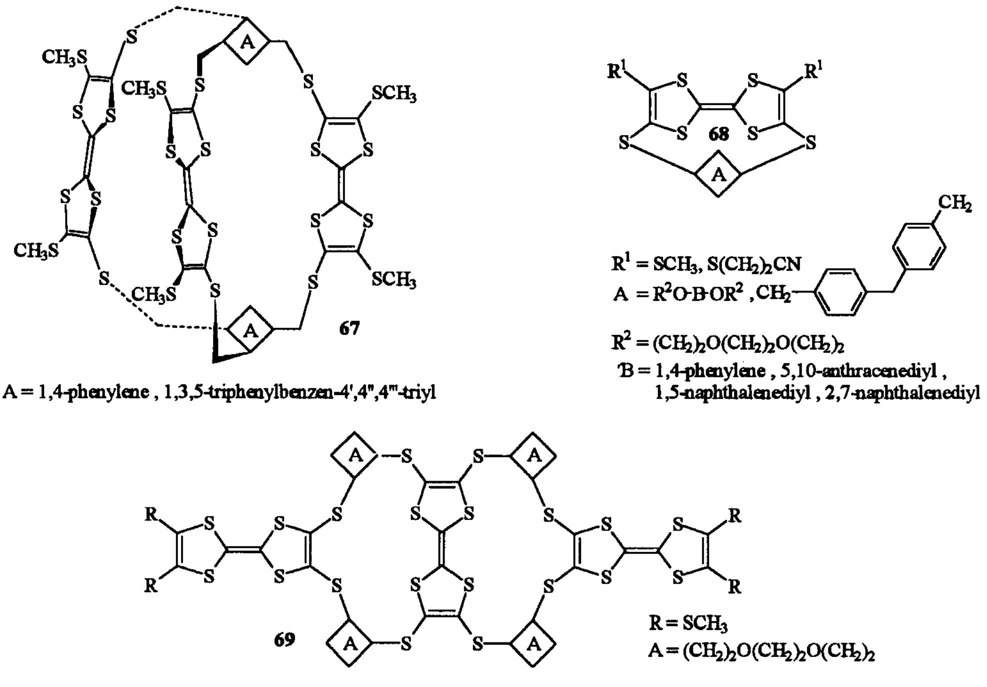
The intramolecular coupling of 4,4-(alkylenedithio)bis(5-methoxycarbonyl-1,3-dithiol-2-one)s with triisopropyl phosphite and subsequent decarboxylation with lithium bromide monohydrate provides a *cis*/*trans* mixture of double-linkaged TTF dimers [357]. A deprotection/realkylation reaction of 2,6(7)-bis(2-methoxycarbonylethylthio)-TSF with cesium hydroxide-alkylenedibromides affords the *cis*/*trans* mixture of the corresponding double-linkaged TSF dimers [358]. Three (*cis*/*cis*, *cis*/*trans*, *trans*/*trans*-twist) of the four possible isomers could be isolated by elaborate fractional crystallization in the case of TTF dimers (X = S, $n = 1, 2, 3, 4$) and TSF dimers (X = Se, $n = 2$) (Scheme 53).

In the TTF dimers **66** with double-linkage in the case of short bridges [A = $(CH_2)_2$, $(CH_2)_3$] only the *cis*-isomer is isolated, but in the case of longer bridges [A = $(CH_2)_2O(CH_2)_2$, CH_2-1,4-phenylene-CH_2] a *cis*/*trans* mixture is formed [359].



SCHEME 53

In the tetrathiafulvalenophanes **67** [360,361], **68** [348,362,363], and **69** [364,365] the flexibility of the molecules is high enough for isomerization. *Cis*/*trans* mixtures are formed and could not be separated because of their slow isomerization in solution probably favoured by traces of acid. Only in the tetrathiafulvalenophane **68** ($R^1 = SCH_3$, $A = CH_2C_6H_4CH_2C_6H_4CH_2$) crystallization from a mixture of dichloromethane/hexane afforded a mixture of two different crystal types, which can be separated easily from each other by mechanical sorting and identified as *cis*- and *trans*-isomers [348].



A = 1,4-phenylene, 1,3,5-triphenylbenzen-4',4'',4'''-triyl

$R^1 = SCH_3, S(CH_2)_2CN$

$A = R^2O\text{-}B\text{-}OR^2, CH_2-$

$R^2 = (CH_2)_2O(CH_2)_2O(CH_2)_2$

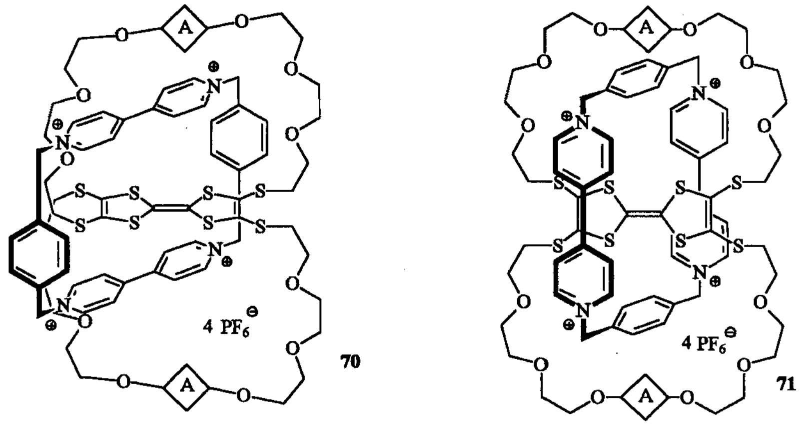
B = 1,4-phenylene, 5,10-anthracenediyl, 1,5-naphthalenediyl, 2,7-naphthalenediyl

$R = SCH_3$

$A = (CH_2)_2O(CH_2)_2O(CH_2)_2$

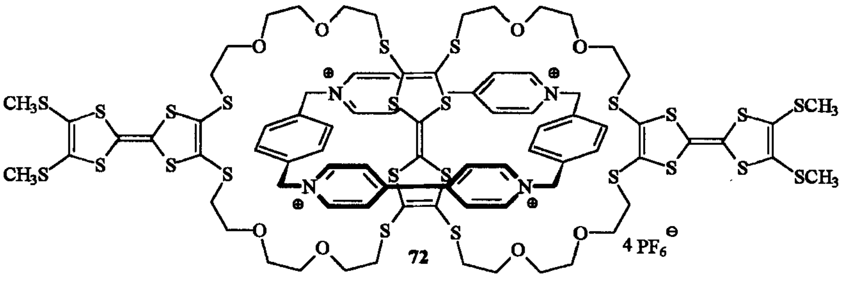
SCHEME 54

In some cases the structure of tetrathiafulvalenophanes can be fixed by forming of catenanes with 1,1'-[1,4-phenylenebis(methylene)]bis-4,4'-bipyridinium bis(hexafluorophosphate). Clamping of the TTF moiety in **70**, **71**, and **72** by bipyridinium tetracation prevents isomerization also in the presence of trifluoroacetic acid [362,364–366].



70 **71**

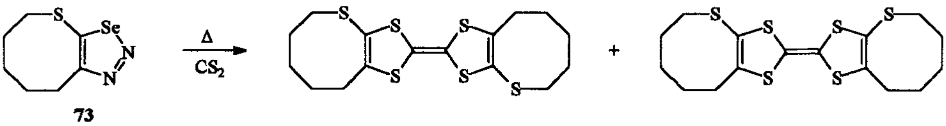
A = 1,4-phenylene, 5,10-anthracenediyl, 1,5-naphthalenediyl, 2,7-naphthalenediyl



72

SCHEME 55

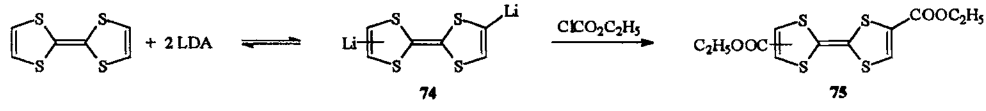
By means of ^{13}C NMR measurements the formation of a 1 : 1 mixture of *cis*- and *trans*-isomer by thermolysis of a substituted 1,2,3-selenadiazole **73** in carbon disulfide could be proved [367].



73

SCHEME 56

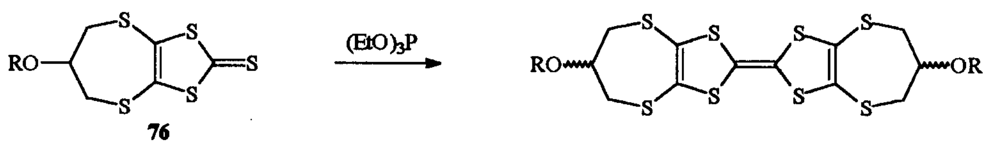
Dilithiation of TTF gave an approximate 1 : 1 mixture of the *cis*- and *trans*-isomers **74** as evident from the ^{1}H NMR spectrum of the reaction products **75**, formed by reaction of **74** with ethyl chloroformate [368].



74 **75**

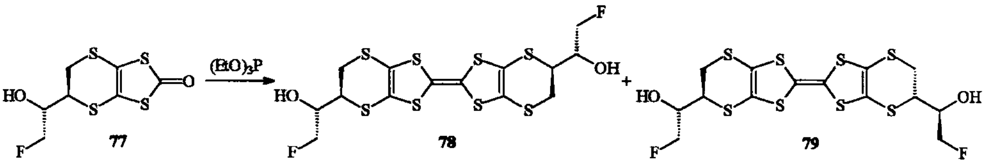
SCHEME 57

The self-coupling of the thiones **76** with triethyl phosphite provides a mixture of diastereoisomers. This was confirmed by ^{1}H NMR data but it was not necessary to separate the diastereoisomers [208].



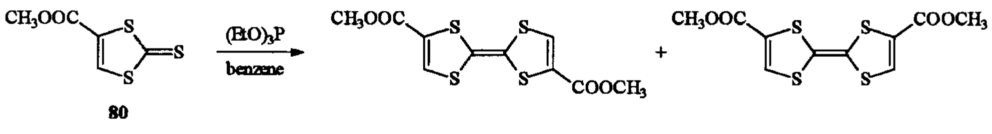
SCHEME 58

Reaction of **77** with neat triethyl phosphite gave a mixture of **78** and **79** which could not be separated. The ^{13}C NMR spectrum shows two sets of signals except for the terminal C atoms in each side-chain. By ^{1}H NMR data the mixture of *cis* and *trans* is 1 : 1 [369].



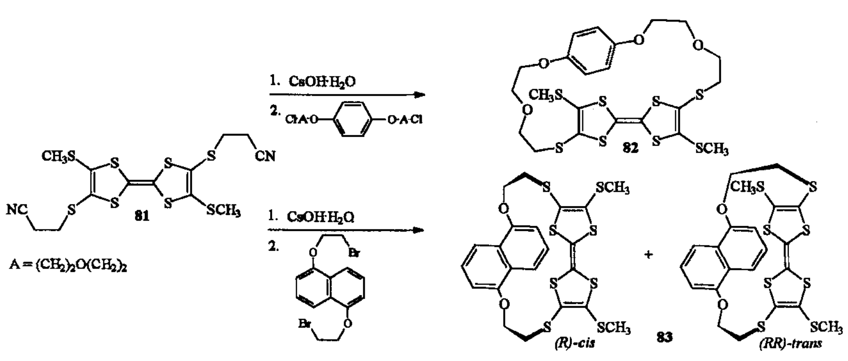
SCHEME 59

In some cases the *cis*/*trans* mixture could be separated. Treatment of 4-carbomethoxy-1,3-dithiole-2-thione **80** with triethyl phosphite in refluxing benzene resulted in the formation of two products which could be separated by their different solubility in benzene [199]. The two products are distinguished by different melting points and small differences in their IR spectra but an assignment to *cis*- and *trans*-isomers has not been given.



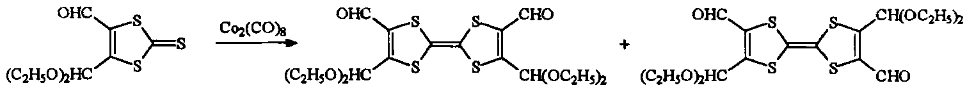
SCHEME 60

Deprotection of a *cis*/*trans* mixture of **81** with cesium hydroxide, followed by realkylation with a bisalkylating agent provides a new TTF, where the *trans*-isomer **82** could be isolated [370]. In an analogous reaction a *cis*/*trans* mixture of tetrathiafulvalene-naphthalenophanes **83** is formed, where the enantiomeric pairs associated with the *cis*-form of the TTF unit as well as one of those associated with the *trans*-form could be isolated by crystallization. But *cis*–*trans* isomerization occurs in solution when either the *cis*- or the *trans*-isomer of the TTF derivative is exposed to light [371].



SCHEME 61

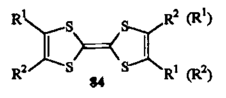
The diacetalized tetraformyl-TTF, prepared by desulfurative coupling of the corresponding thione with dicobalt-octacarbonyl, is obtained as a mixture of essentially equal amounts of the *cis*- and *trans*-isomers [205]. The *cis*-isomer is separated by selective solubilization in ether and subsequent column chromatography. The *trans* structure has been confirmed by X-ray analysis. No *cis–trans* isomerization is observed under the influence of acids on the *cis*-isomer. This is in contrast to the above 5,4′-di(4-chlorphenyl)-4,5′-di(methylthio)tetrathiafulvalene.



SCHEME 62

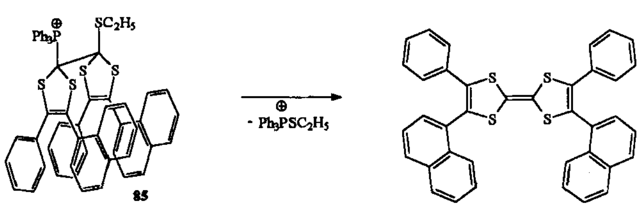
Bulky substituents modify the properties of *cis*- and *trans*-isomers so much that a separation can be carried out based on their different solubilities in TTF **84** [280,372,373].

2-(Ethylthio)-1,3-dithiolium perchlorates bearing bulky substituents yield with triphenylphosphine (method F) in acetonitrile under kinetic-controlled conditions (room temperature) only the *cis*-isomer. Intermediate **85**, affording the TTF, could be stabilized by π–π-interactions between corresponding substituents and thus be kinetically preferred. At higher temperatures the *trans*-isomer is also formed, where the ratio of the *cis*- and *trans*-isomers corresponds to the same ratio of the thermal isomerization of the *cis*-isomer under comparable conditions. Probably the formed *cis*-isomer isomerizes thermally.



84

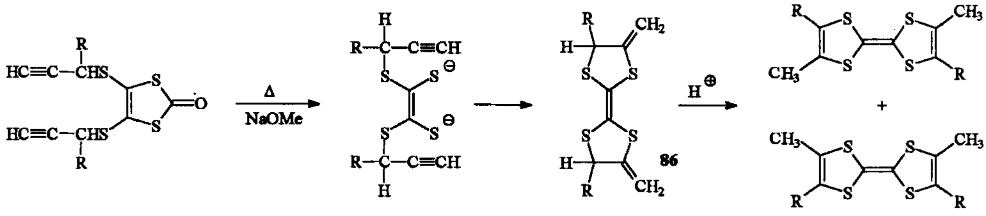
$R^1 = CH_3, C_6H_5$
$R^2 =$ 5,6,7,8-tetrahydro-2-naphthalenyl, 1-naphthalenyl, 2-naphthalenyl, 4-biphenylyl, 3-acenaphthenyl, 5-acenaphthenyl
$R^1, R^2 =$ 3,4-dihydrophenanthreno



SCHEME 63

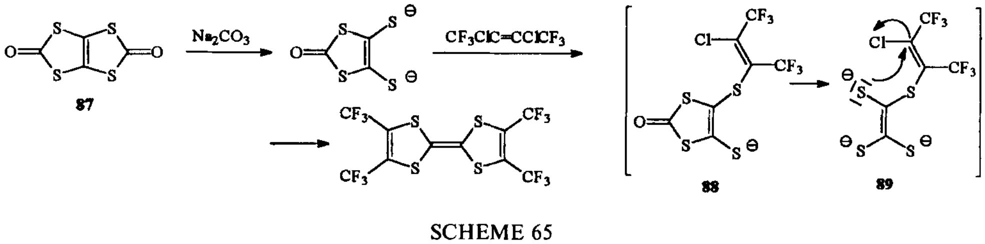
Corresponding 1,3-dithiole-2-thiones provide with triethyl phosphite (method B) in non-polar solvents (xylene, toluene) only the *cis*-isomers. In polar solvents (acetonitrile, dichloroethane) *trans*-isomers are also formed. In the reaction of 2*H*-1,3-dithiolium salts with tertiary amines the ratio of isolated *cis*- and *trans*-isomers is not 1 : 1 and depends on the bulkiness of the tertiary amine. These observations exclude in these three reactions a carbene mechanism for the dimerization of the 1,3-dithiole units to tetrathiafulvalenes [280].

In an alternative synthesis cyclization of 4,5-bis(propargylthio)-1,3-dithiol-2-one to the *cis*-isomer was expected due to the *cis* relationship of the sulfide groups in the intermediate. However, the resulting dimethylenetetrahydro-TTF **86** are oils, making X-ray analysis unfeasible. After isomerization with 4-toluenesulfonic acid in refluxing benzene a mixture of *cis*- and *trans*-isomers is formed, as an X-ray structure determination proves [159]. The *cis*/*trans* mixture is probably formed by protonation of the central double bond, followed by isomerization.



SCHEME 64

In a similar nucleophilic substitution reaction tetrakis(trifluoromethyl)-TTF is formed by alkaline hydrolysis of 1,3,4,6-tetrathia-pentalene-2,5-dione **87** in the presence of 2,3-dichlorohexafluoro-2-butene under phase transfer conditions [374]. It is proposed that the intermediate **88** is formed after initial attack of the alkyl halide by the dianion. The extremely electron-withdrawing substituent could facilitate the opening of the second ring and stabilize the resulting trianion **89**. After intramolecular cyclization and reaction with a second molecule of alkyl halide the tetrakis(trifluoromethyl) TTF would be formed. The formation of the TTF derivative with an *exo*-double bond should be energetically preferable to the isomeric dithiine.



SCHEME 65

2. SYNTHESIS OF DITHIADISELENAFULVALENES (DTDSF), 1,3-THIASELENOLE-2-THIONES AND -SELONES

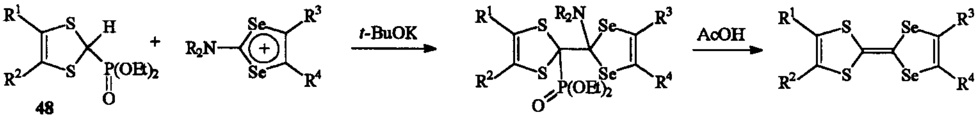
DTDSF exist in two isomeric forms; in the isomer **90** each ring contains identical heteroatoms (1,3-dithia-1′,3′-diselenafulvalenes), in the isomer **91** each ring contains different heteroatoms (1,1′-dithia-3,3′-diselenafulvalenes) with the possibility of a *cis*- and a *trans*-form.

The 1,3-dithia-1′,3′-diselenafulvalenes **90** are prepared by cross-coupling of the appropriate 1,3-dithiole and 1,3-diselenole derivatives with trimethyl or triethyl phosphite. In addition to the desired DTDSF the symmetrical self-coupling products are formed. Separation of the symmetrical self-coupling products is accomplished by column chromatography on silica, followed by repeated preparative gel permeation chromatography [375,376].

90 **91**

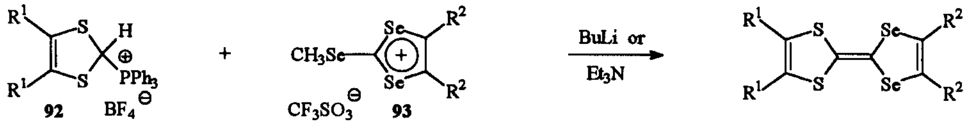
SCHEME 66

In analogy to the synthesis of unsymmetrical TTF derivatives [242] the DTDSF **90** are obtained in pure form and without by-products (TTF and TSF) by reaction of (1,3-dithiol-2-yl)ethyl phosphonate **48** with 2-amino-1,3-diselenolium salts in the presence of strong bases, followed by addition of acetic acid [377–379].



SCHEME 67

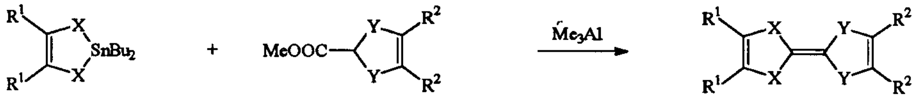
In a similar way the 1,3-dithiol-2-ylidenephosphoranes of **92** form with 2-alkylseleno-1,3-diselenolium salts **93** the corresponding DTDSF [255,380].



$R^1 = Se(CH_2)_2CN$, $O(CH_2)_2O$, $R^2 = CH_3$

SCHEME 68

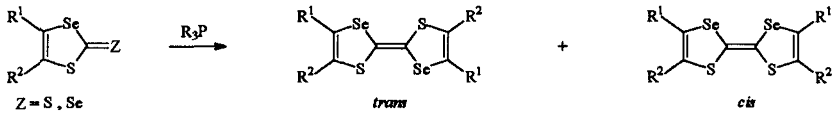
In an analogous manner to organoaluminium reagents (see Section 1.9) organotin thiolates or -selenolates react with the esters of 1,3-dithioles or 1,3-diselenoles in the presence of trimethylaluminium and provide the unsymmetrical substituted DTDSF **90** [307,309,310].



$R^1 = CH_3$, X = Se ; $R^2 = S(CH_2)_2S$, Y = S
$R^1 = S(CH_2)_2S$, X = S ; $R^2 = (CH_2)_3$, Y = Se
$R^1 = CH_3$, $(CH_2)_3$, X = Se; R^2 = thiadiazolo, Y = S

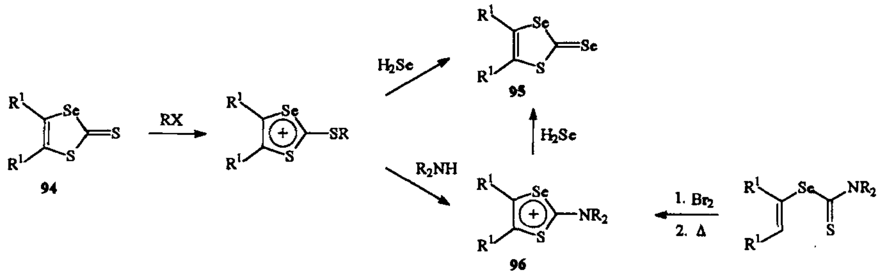
SCHEME 69

The synthesis of symmetrical DTDSF **91** 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/trans* mixture of isomers. The mixture cannot be separated at all [381,382]. The existence of both isomers is proved by ^{1}H NMR spectroscopy [223,373,381,383].



SCHEME 70

Among the unsubstituted compounds the reaction works only with 1,3-thiaselenole-2-selone [381,382]. Selones normally give higher yields than the corresponding thiones [373,384]. Therefore 1,3-thiaselenole-2-thiones **94** are converted into the 1,3-thiaselenole-2-selones **95**. This occurs in the case of the methyl substituted compound **94** by alkylation and treatment of the so formed thiaselenolium salt with hydrogen selenide [223], or in the case of cycloalkyl substituted and benzo-annelated derivatives [384] as well as unsubstituted 1,3-thiaselenole-2-thione [382] by conversion to a 2-amino-1,3-thiaselenolium salt **96** and following treatment with hydrogen selenide [382,384]. 2-Amino-1,3-thiaselenolium salt **96** are also synthesized by oxidative cyclization of alkenyl *N*,*N*-dialkylthioselenocarbamates with bromine and thermal elimination of hydrogen bromide [385].

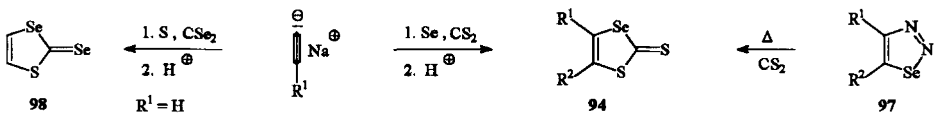


SCHEME 71

Methyl-, phenyl- and unsubstituted 1,3-thiaselenole-2-thione **94** is prepared in a one-step synthesis by addition of selenium and carbon disulfide to the corresponding acetylide [386,387].

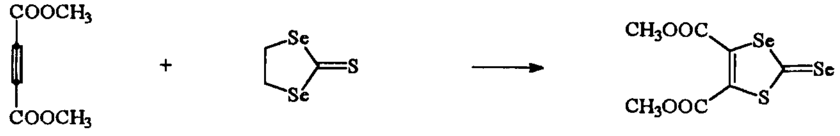
Thermolysis of the corresponding 1,2,3-selenadiazoles **97** in excess carbon disulfide affords the unsubstituted [382], the cycloalkyl substituted [99,384,388] and the benzo-annelated [384] 1,3-thiaselenole-2-thione **94**.

The 1,3-thiaselenole-2-selones **93** can also be obtained directly. The unsubstituted compound **98** is formed in low yield (8%) from sodium acetylide, sulfur and carbon diselenide [387].



SCHEME 72

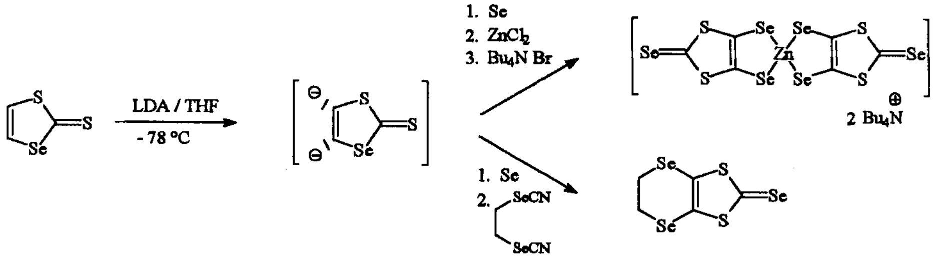
Treatment of 1,3-diselenolane-2-thione with dimethyl acetylenedicarboxylate gives the corresponding selone ester **99** in good yield (70%) [382,389].



99

SCHEME 73

The synthesis of selenosubstituted 1,3-thiaselenole-2-thiones is not possible by lithiation of the thione and subsequent selenation. During the lithiation selenation sequence a selenium–sulfur scrambling occurs and the corresponding 1,3-dithiole-2-selone derivatives are formed [154].

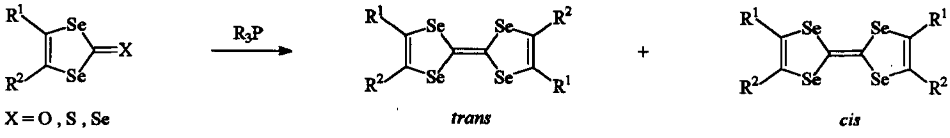


SCHEME 74

DTDSF and their data are summarized in Table XIV.

3. SYNTHESIS OF TETRASELENAFULVALENES (TSF)

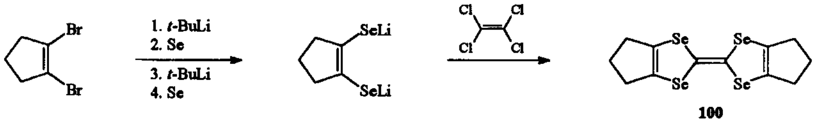
TSF are obtained by coupling of 1,3-diselenole-2-thiones, -selones, or -ones with trivalent phosphorus compounds.



SCHEME 75

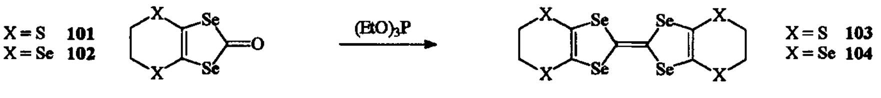
If differently substituted 1,3-diselenole derivatives are used, a mixture of *cis*/*trans*-isomers is formed. Only in one case could such a mixture be separated on the basis of solubility differences of the isomers [390].

Only tetrakis(trimethylsilyl)tetraselenafulvalene has been synthesized by reaction under high pressure (5–6 kbar) between bis(trimethylsilyl)acetylene and carbon diselenide in moderate yield (20%) [271]. Hexamethylenetetraselenafulvalene **100** was obtained by a synthesis analogous to that of the tetratellurafulvalenes [391]. This route was also successful if the intermediate *cis*-ethene-1,2-diselenolate is treated with tetrachloroethene at −78°C, followed by slowly warming to room temperature and then heating it to 45°C. Indeed the yield of the unsubstituted TSF is only 1% [392].



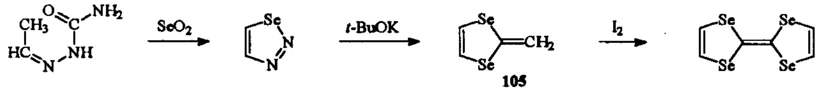
SCHEME 76

In the dechalcogenation reaction of 1,3-diselenole-2-thiones, -selones, or -ones with trivalent phosphorus compounds the 1,3-diselenole-2-selones give mostly higher yields of TSF than the corresponding 1,3-diselenole-2-thiones [221,393]. With 1,3-diselenole-2-thiones an unexpected selenium–sulfur scrambling can occur, so that triselenathiafulvalenes are formed as by-products [393]. The synthesis of bis(ethylenedithio)- and bis(ethylenediseleno)tetraselenafulvalene **103** and **104**, respectively, is successful only with 4,5-ethylenedithio- or 4,5-ethylenediseleno-1,3-diselenol-2-one **101** and **102**, respectively [202,394]. The corresponding selones do not react with triethyl phosphite.



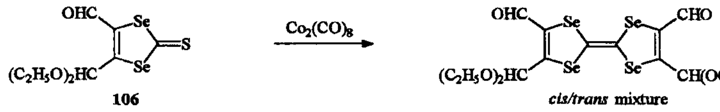
SCHEME 77

In a yield of about 30% TSF is obtained without use of the toxic CSe_2 in a three-step reaction. Acetaldehyde semicarbazone forms with selenium dioxide 1,2,3-selenadiazole which in turn reacts with potassium *t*-butoxide in DMF/*t*-BuOH and provides fulvene **105**. Addition of a mixture of iodine and morpholine in DMF to a solution of **105** furnishes TSF [395].



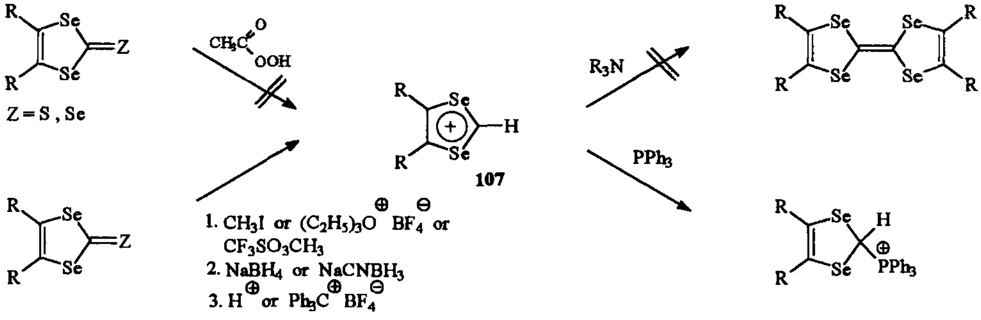
SCHEME 78

In analogy to the synthesis of TTF [396] the corresponding TSF are formed upon reflux of 1,3-diselenole-2-selones in toluene with dicobaltoctacarbonyl. In the case of the monoacetalized **106** a mixture of practically equal amounts of the *cis*- and *trans*-isomer of the TSF is obtained and separated by silica thick layer chromatography [397]. The stereochemistry was assigned by comparison with X-ray structures of the corresponding TTF [398].



SCHEME 79

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 [200]. The oxidation of 1,3-diselenole-2-thiones or -selones fails to give the desired 1,3-diselenolium salts **107** [221,399,400]. The 1,3-diselenolium salts **107** are available by alkylation of 1,3-diselenole-2-thiones or -selones, reduction with sodium borohydride or sodium cyanoborohydride and treatment with tetrafluoroboric acid [401] or trityl tetrafluoroborate [402,403], the reaction of **107** with trialkylamines provides only elemental selenium as precipitate [221]. With triphenylphosphine the corresponding Wittig reagent can be prepared [403] and reacted with a variety of functionalized aldehydes to form conjugated tetraselenafulvalenes (see Section 6).



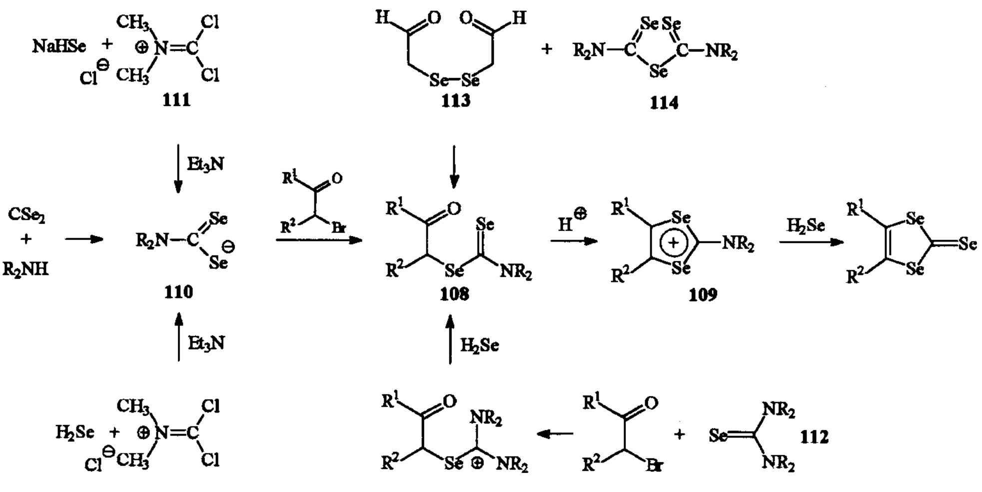
SCHEME 80

TSF and their data are summarized in Table B3.

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

The required 1,3-diselenole-2-selones can be prepared by various methods. In analogy to 1,3-dithiole-2-thiones [82–84], 1,3-diselenole-2-selones are synthesized by ring closure of *β*-keto *N*,*N*-dialkyldiselenocarbamates **108** with concentrated sulfuric acid at room temperature and subsequent treatment of the so formed 2-(*N*,*N*-dialkylamino)-1,3-diselenolium salts **109** with hydrogen selenide in 70% methanol [400,404]. Before reaction with hydrogen selenide, the 2-(*N*,*N*-dialkylamino)-1,3-diselenolium hydrogen sulfates **109** are converted to well crystallizing, but explosive perchlorates [400,404,405]. Less dangerous is the handling of tetrafluoroborates [406] or hexafluorophosphates [407,408].

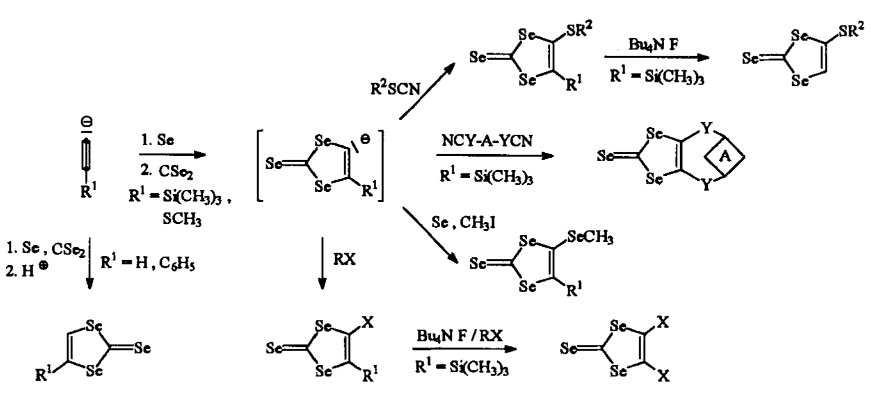
Alkyl [400,404], aryl [400], and aralkyl substituted [405] *β*-keto *N*,*N*-dialkyldiselenocarbamates **108** are generated by treatment of the corresponding α-bromo ketones with *N*,*N*-dialkyldiselenocarbamates **110**. In the synthesis of alkyl derivatives a convenient solvent is dichloromethane [400,409,410] or *N*,*N*-dimethylformamide [407] and for aralkyl substituted compounds methanol [411]. The *N*,*N*-dialkyldiselenocarbamate **110** is prepared by the reaction of carbon diselenide with a dialkylamine (e.g. piperidine, morpholine, pyrrolidine) [400,412]. Since carbon diselenide is an extremely fetid reagent and only produced in 30% yield via the reaction of dichloromethane with selenium at 600°C [413], it is better to treat hydrogen selenide with dichloromethylene *N*,*N*-dimethylammonium chloride **111** [414] in the presence of triethylamine [410,415] or piperidine [409]. 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 situ* [407]. Synthesis of β-keto *N*,*N*-dialkyldiselenocarbamates **108** without use of carbon diselenide is possible by reaction of *N*,*N*,*N*′,*N*′-tetramethylselenourea **112** with α-bromo ketones, followed by treatment with hydrogen selenide [416]. The disadvantage of this method is that only fair yields of **108** are obtainable. The reaction between the corresponding diselenide **113** and bis(*N*,*N*-dialkylselenocarbamoyl) selenides **114** in the presence of 4-toluenesulfonic acid in chloroform leads to the β-formyl *N*,*N*-dialkyldiselenocarbamates **108**, which permit access to the unsubstituted 1,3-diselenole-2-selone [408].



SCHEME 81

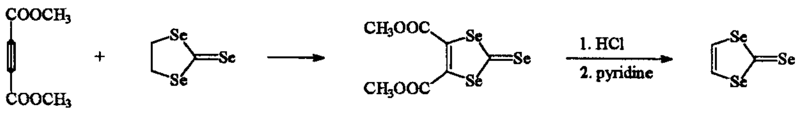
The unsubstituted and 4-phenyl substituted 1,3-diselenole-2-selone are prepared more easily in analogy to 1,3-dithiole-2-thione [110] by addition of selenium and carbon diselenide to the corresponding sodium acetylides [387,417]. Experimental modifications of this conversion (reaction in the presence of tetramethylethylenediamine in THF with *n*-BuLi at −78°C, subsequently with selenium at 0°C and then with carbon diselenide at −90°C) provides higher yields and enables the extension to monosubstituted alkynes [111,113,115] or alkylene bridged dialkynes [418].

In the same way alkylchalcogeno- or alkylenedichalcogeno-substituted 1,3-diselenole-2-selones are synthesized by successive treatment of trimethylsilylacetylene with *n*-BuLi, selenium, carbon diselenide, and finally alkyl thiocyanate or selenium and then alkyl halides [114,218,358,419] or α,ω-bis(chalgogenocyanato)alkanes [420] respectively. In this one-pot reaction the formed intermediate 4-trimethylsilyl-1,3-diselenole-2-selone anion is also halogenated by subsequent quenching with hexachloroethane or 1,2-dibromo-1,1,2,2-tetrafluoroethane or perfluoroiodohexane affording the corresponding 4-halo-5-trimethylsilyl-1,3-diselenole-2-selones. The reaction proceeds also by starting from *cis*-1-bromopentene and forms the 4-halo-5-methyl-1,3-diselenole-2-selones [421].



SCHEME 82

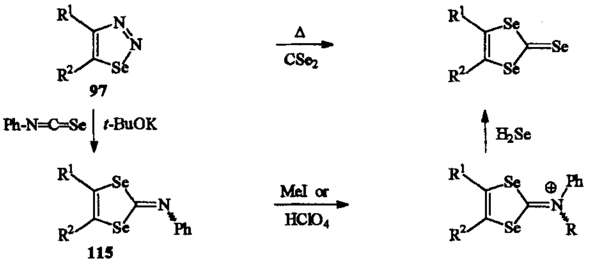
In a multi-step synthesis the parent compound is obtained, also in analogy to 1,3-dithiole-2-thione [116] in high yield (each step over 60%) by reaction of 1,3-diselenolane-2-selone with dimethyl acetylenedicarboxylate, followed by hydrolysis and decarboxylation [422].



SCHEME 83

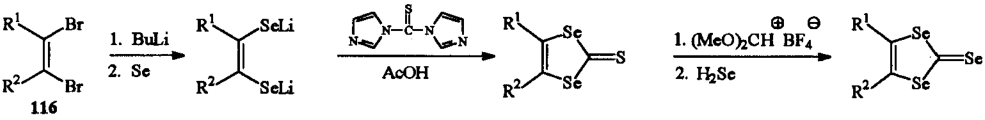
Cycloalkyl substituted (R^1, $R^2 = CH_2CH_2CH(CH_3)$ [99], R^1, $R^2 = CH_2SCH_2$ [423]) and benzo-annelated [424] 1,3-diselenole-2-selones are formed in moderate (10–35%) and relatively good (70%) yields, respectively, by thermolysis of the corresponding 1,2,3-selenadiazoles **97** in the presence of excess carbon diselenide. Thermolysis of 1,2,3-selenadiazoles **97** takes place under appreciably milder conditions (reflux in toluene, xylene, carbon diselenide) than the thermolysis of 1,2,3-thiadiazoles **8**. In the presence of potassium *t*-butoxide thermolysis of the unsubstituted 1,2,3-selenadiazole **97** already occurs at 0°C and gives 1,3-diselenole-2-selone in 40% yield [402].

Phenylisoselenocyanate reacts with 1,2,3-selenadiazoles **97** ($R^1 = H$, Me, Ph, $R^2 = H$) in the presence of potassium *t*-butoxide in DMF/*t*-BuOH and provides the corresponding 2-phenylimino-1,3-diselenoles **115**. The diselenoles **115** undergo further transformation with methyl iodide or perchloric acid to form iminium salts, which can be converted to 1,3-diselenole-2-selones by reaction with hydrogen selenide [425].



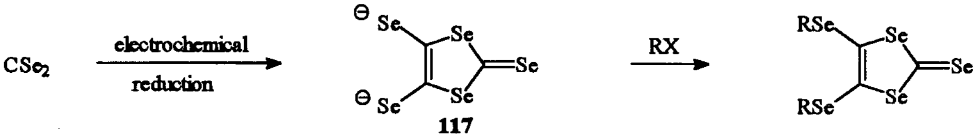
SCHEME 84

Benzo-annelated [426] and heterocyclo substituted [173–175] 1,3-diselenole-2-selones are prepared in analogy to the corresponding sulfur compounds [172–175] from the 1,2-dibromo derivatives **116**. These are lithiated with *t*-butyllithium or via a 1,3-phenylene-mercury compound [427] with lithium, then treated with selenium powder; subsequently 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.



SCHEME 85

Electrochemical reduction of carbon diselenide at 40°C provides the 4,5-diselenolate-1,3-diselenole-2-selone **117**, which can be alkylated with alkylating agents [394]. The same product is also afforded by reduction with potassium naphthalenide in tetrahydrofuran [394].

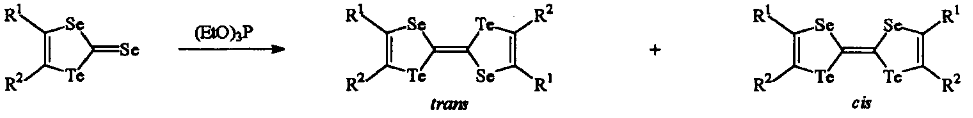


SCHEME 86

The 4,5-diselenolate-1,3-diselenole-2-selone **117** is formed not only by electrochemical reduction of carbon diselenide but also by reduction of carbon diselenide with sodium metal in organic solvents. 4,5-Diselenolate-1,3-diselenole-2-selone is isolated as bis(tetraphenylphosphonium) bis(2-selono-1,3-diselenole-4,5-diselenolato)zincate (II) in a yield of 15% in diglyme and 2% in dimethyl sulfoxide [428]. This complex is also formed by reaction of 1,3-diselenole-2-selone with LDA and selenium and subsequent treatment with zinc chloride and tetraphenylphosphonium bromide [429]. A selenium–sulfur scrambling occurs by the reaction of the 1,3-diselenole-2-thione with LDA and selenium followed by treatment with zinc chloride [154].

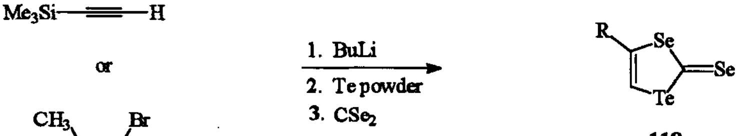
4. SYNTHESIS OF DISELENADITELLURAFULVALENES (DSDTeF), 1,3-SELENATELLUROLE-2-SELONES

DSDTeF (1,1′-diselena-3,3′-ditellurafulvalenes) are synthesized by refluxing of the corresponding 1,3-selenatellurole-2-selones with triethyl phosphite in benzene or toluene, where a mixture of the *cis*- and *trans*-isomers are formed. The geometrical isomers could not be separated by conventional purification methods. Only in the case of the dimethyl derivative the *trans*-isomer precipitated in pure form by recrystallization from benzene [430].



SCHEME 87

Analogously to the 1,3-thiaselenole-2-thiones the unsubstituted and 5-methyl-1,3-selenatellurole-2-selone **118** is prepared in a one-step synthesis by addition of tellurium and carbon diselenide to the corresponding acetylide [430].



118 R = H, CH_3

SCHEME 88

DSDTeF and their data are summarized in Table B4.

5. SYNTHESIS OF TETRATELLURAFULVALENES (TTeF)

Tetratellurafulvalenes are synthesized in the following way: 1,2-dibromo derivatives **116** are lithiated with *t*-butyllithium, then treated with tellurium powder and finally with tetrachloroethene [174,175,431–433]. Yields vary between 10 and 75%.

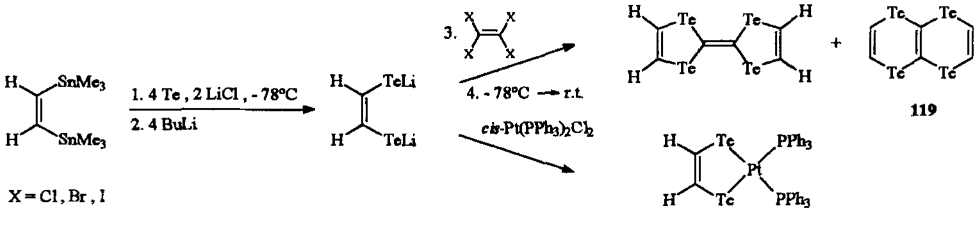
116

SCHEME 89

The synthesis of TTeF has been improved by the development of a five-step, one-pot reaction starting from *cis*-1,2-bis(trimethylstannyl)ethene [434,435]. After two consecutive metallations the 1,2-(dilithioditelluro)ethene formed (trapping with *cis*-Pt$(PPh_3)_2Cl_2$ gives $Pt(Te_2C_2H_2)(PPh_3)_2$ in 28% yield) was treated not with tetrachloroethene [434], but with tetrabromoethene [435]. This greatly improves the ease of isolation, lowers the yield of undesirable by-products, and increases the purified yield of TTeF to 12% (tetrachloroethene gives a 5% yield of pure TTeF and tetraiodoethene < 1% yield of pure TTeF).

Further improvements are the result of a systematic synthetic study. In a one-step reaction provides the *cis*-1,2-bis(trimethylstannyl)ethene by reaction with freshly prepared microcrystalline tellurium, a twofold excess of *n*-BuLi, lithium chloride as an additive and slow addition of tetrabromoethene the TTeF in a yield of 26% [436].

One by-product in the reaction of 1,2-(dilithioditelluro)ethenes with tetrachloroethene is the corresponding 1,4,5,8-tetra-telluratetraline **119** [324,434].

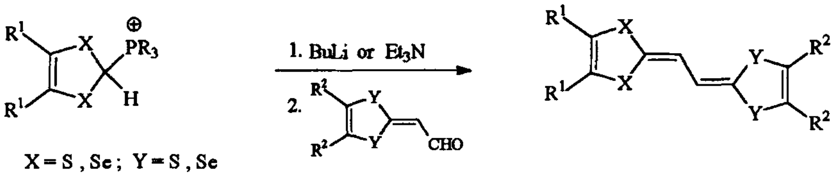


SCHEME 90

TTeF and their data are summarized in Table B5.

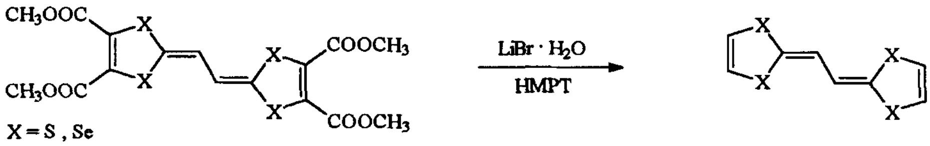
6. SYNTHESIS OF CONJUGATED TETRATHIA- AND TETRASELENAFULVALENES

Essentially the synthesis of the ethanediylidene derivatives is based on the Wittig-type reaction of a phosphorane [234,437,438] or a phosphonate anion [439–444] with the appropriate aldehyde.



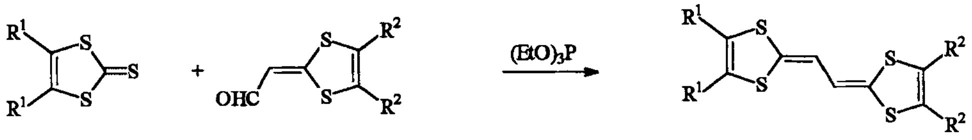
SCHEME 91

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 [234,437].



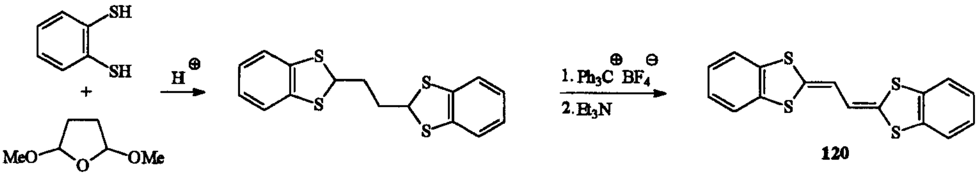
SCHEME 92

Analogously to TTF the TTF vinylogues are also formed by triethyl phosphite mediated coupling of 1,3-dithiole-2-thiones with 2-formylmethylene-1,3-dithioles. The reaction proceeds smoothly, is independent of the substituent on the starting material, provides no homo-coupling by-products and does not require so much effort for the synthesis of the starting material like the former Wittig-type reaction [445].



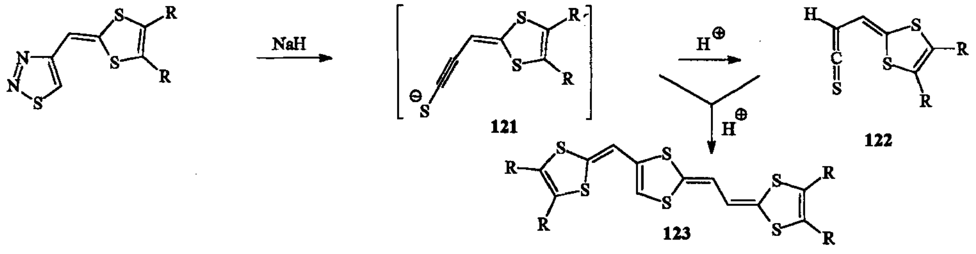
SCHEME 93

The benzo-annelated compound **120** is prepared by treatment of 1,2-benzodithiole with 2,5-dimethoxytetrahydrofuran in acidic solution, followed by hydride abstraction and deprotonation [446,447].



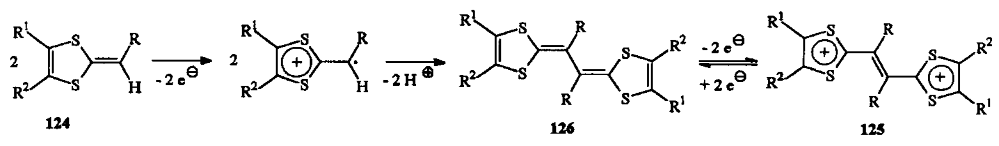
SCHEME 94

Base-mediated thermolysis of 1,2,3-thiadiazoles **8** in carbon disulfide provides the corresponding 4-substituted 1,3-dithiole-2-thiones (see Section 1.1). 1,4-Dithiafulvenyl substituted 1,2,3-thiadiazoles form under these conditions in the absence of carbon disulfide by the reaction of the intermediates alkyne-1-thiolates **121** and thioketenes **122** the ethanediylidene derivatives **123** [171,448].



SCHEME 95

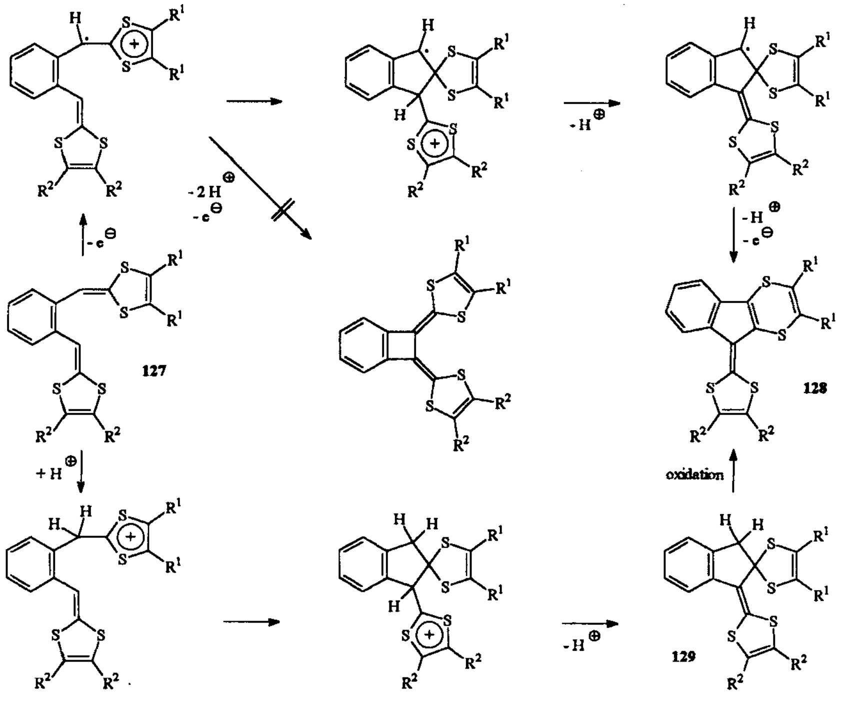
The oxidative dimerization of 1,4-dithiafulvenes **124** with MnO_2, PbO_2, *p*-benzoquinones, tris(4-bromophenyl)aminium hexachloroantimonate or electrochemically provides the corresponding dications **125**, which can be reduced to the ethanediylidene derivatives **126** with zinc dust, with mercury or electrochemically. The first step in this reaction is the formation of the radical cation with subsequent dimerization to the dimer **126**. The dimer **126** has a lower oxidation potential than the 1,4-dithiafulvene **124** and is oxidized to the dication **125**. The dication **125** can be reduced to the ethanediylidene derivatives **126** [442,449–461]. Investigations by cyclic voltammetry at low and high scan rates for a series of substituted 1,4-dithiafulvenes confirmed this mechanism of the oxidative dimerization to form vinylogues TTF [462].



SCHEME 96

Some TTF analogues are synthesized with two or more 1,3-dithiol-2-ylidene moieties separated by olefinic bonds [463,464].

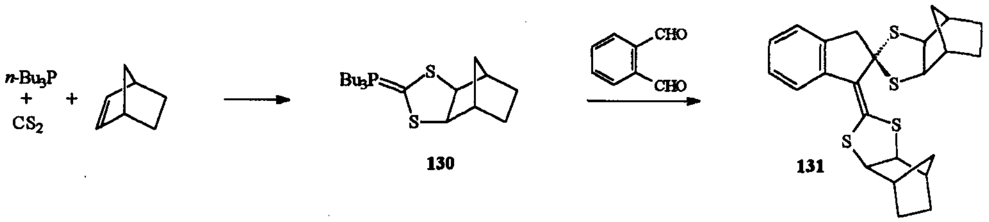
Bromination of 1,2-phenylenebis[2,3-bis(methoxycarbonyl)-1,4-dithiafulven-6-yl] **127** ($R^1 = R^2 = COOCH_3$) with bromine in carbon tetrachloride does not lead analogously to oxidation of diphenyldithiafulvene **124** to a benzocyclobutene-derived molecule, but provides the dithiinofulvenetetraester **128** (confirmed by X-ray analysis). For the formation of **128** a pathway with oxidation and deprotonation steps and a final S–C 1,2-shift is proposed [465]. However, if only 0.2 equivalents of bromine are used for the oxidation of **127**, the formation of **129** is observed (confirmed by X-ray analysis). **129** can be further oxidized to **128** with an excess of bromine. **129** is also formed by an acid mediated or electrochemically induced intramolecular cyclization of **127**. Because in the electrochemical reaction for the complete conversion of **127** only 0.05 faradays per mol are required and the conversion is inhibited in the presence of 2,4,6-collidine, it is concluded that protons could be also responsible for the catalytic step. **129** could be an intermediate in the formation of **128** from **127** [466,467].



SCHEME 97

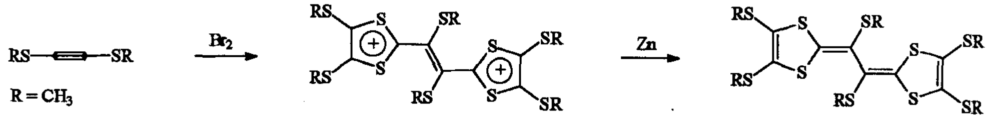
The mass spectra of **127** and **129** are identical, suggesting that the cyclization can also occur under the conditions of recording the electron impact ionization mass spectra [468].

Norbornene gives with the adduct between carbon disulfide and tributylphosphine the 1,3-dithiolan-2-ylidenephosphorane **130** which can be trapped by a Wittig reaction with phthalaldehydes. In the case of 1,3- or 1,4-dialdehydes the expected bisdithiolanes are formed, but the 1,2-dialdehyde yields, analogously to **129**, the rearrangement product **131** [263].



SCHEME 98

Oxidation of bis(methylthio)acetylene with bromine leads to the dication of the corresponding ethanediylidene-2,2′-bis(1,3-dithiole), which can be reduced with zinc to the parent compound [469].



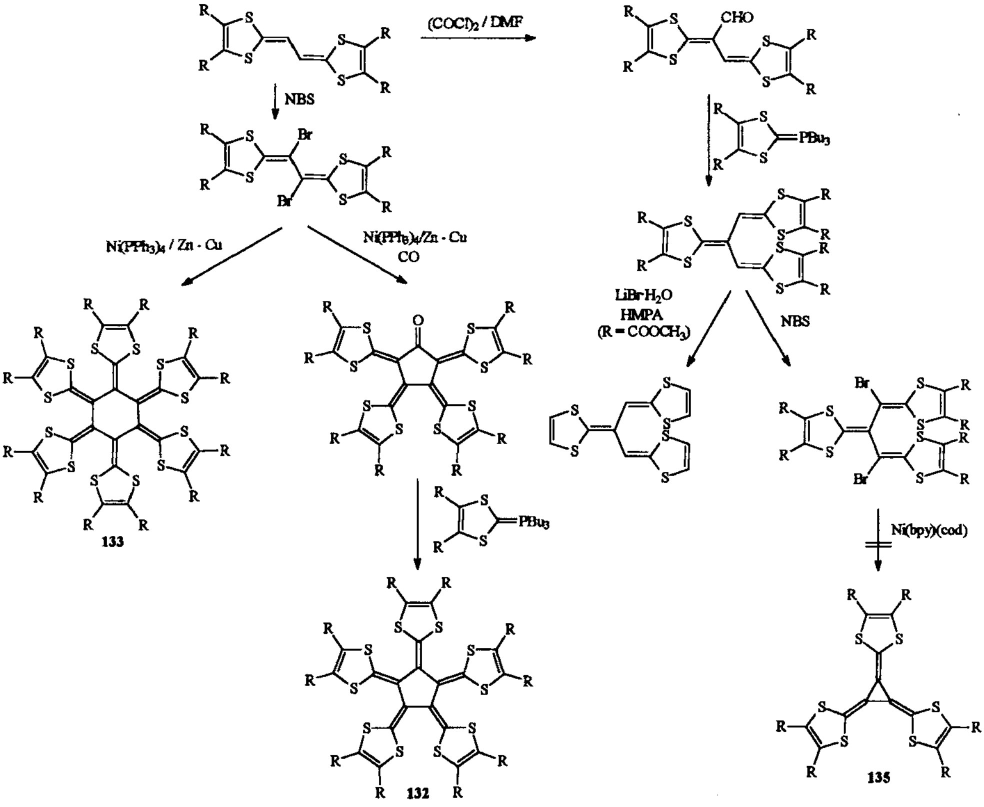
SCHEME 99

Starting from ethanediylidene-2,2′-bis(1,3-dithioles) [5]- and [6]-radialenes **132** and **133** (R = COOMe, $(CH{=}CH)_2$) are obtained in reasonable yields by bromination with *N*-bromosuccinimide, followed by treatment with a $Ni(PPh_3)_4$ complex and Zn–Cu coupling in the presence or absence of carbon monoxide, respectively [470–472]. Reaction of the substituted tris(1,3-dithiol-2-ylidene)propane and tetrakis(1,3-dithiol-2-ylidene)butane (R = COOMe) with lithium bromide monohydrate in hexamethylphosphoramide afforded the unsubstituted derivatives, both in 80% yield [473].

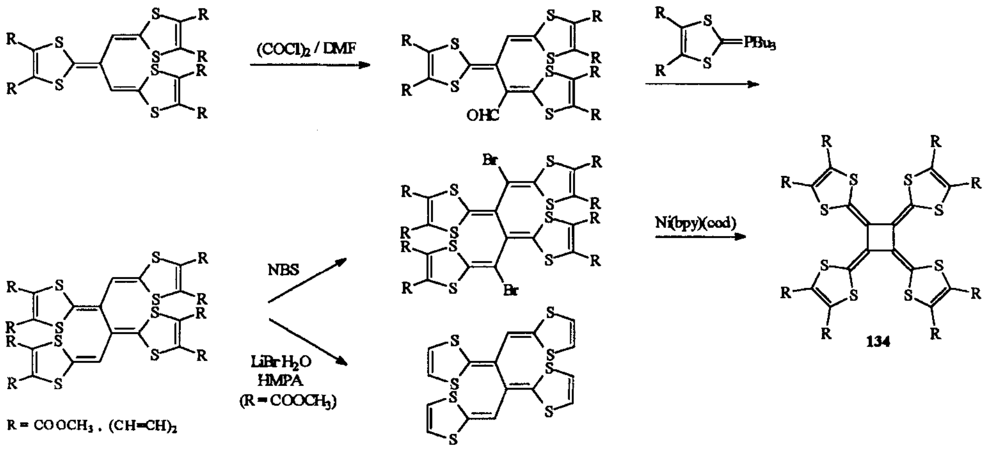
The [4]-radialene **134** (R = COOMe) is obtained in very low yield (3%) from ethanediylidene-2,2′-bis(1,3-dithioles) by two consecutive Vilsmeier reactions with oxalyl chloride/DMF and Wittig reactions with a phosphorane, then bromination with *N*-bromosuccinimide and treatment with a zerovalent Ni(bpy)(cod)-complex [473].

The [3]-radialene **135** (R = COOMe, $(CH{=}CH)_2$) has not yet been prepared in this way [473].

X-ray structure analyses of the [4]-, [5]- and [6]-radialenes indicated not a planar, but rather a three-dimensional structure [470].

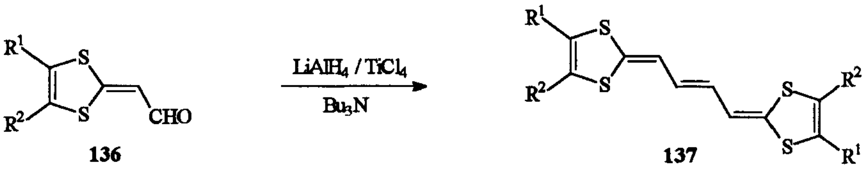


SCHEME 100



SCHEME 101

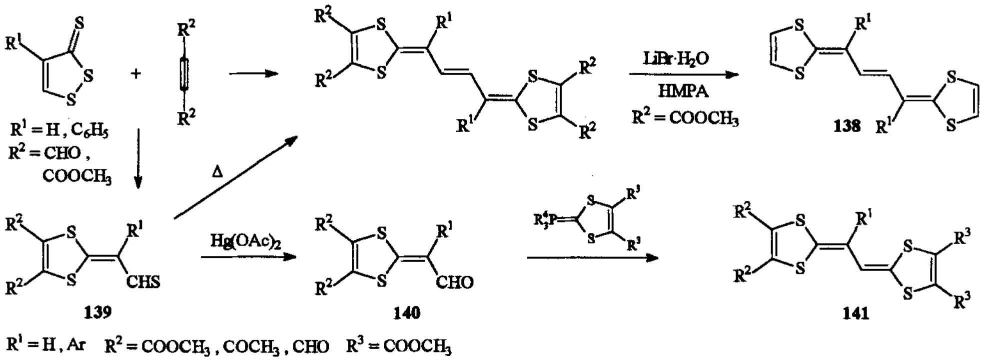
The unsubstituted and the benzo-annelated compound in the series of 1,4-butenediylidene derivatives **137** are obtained by reduction of the corresponding 2-formylmethylene-1,3-dithiole **136** with lithium aluminium hydride in the presence of titanium tetrachloride and tributylamine in tetrahydrofuran [474].



SCHEME 102

The unsubstituted compound **138** ($R^1 = H$) is also formed by treatment of 1,2-dithiole-3-thione with dimethyl acetylene-dicarboxylate in benzene, followed by decarbomethoxylation with lithium bromide monohydrate in hexamethylphosphoramide [474]. In some cases the formed intermediates 2-thioformylmethylene-1,3-dithioles **139** could be isolated. Further conversion of these intermediates into the 2-formylmethylene-1,3-dithioles **140** by desulfurization with mercury(II)acetate and following Wittig olefination with 1,3-dithiol-2-ylidenephosphoranes affords unsymmetrical substituted ethanediylidene derivatives **141**. Thermolysis of 2-thioformylmethylene-1,3-dithioles **139** in xylene provides symmetrical substituted 1,4-butenediylidenes [269].

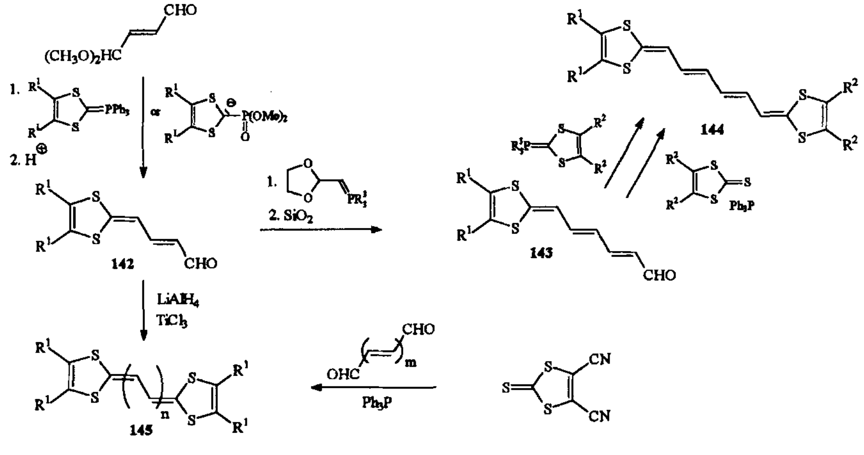
In the same way substituted derivatives can be obtained by reaction of substituted 1,2-dithiole-3-thiones with acetylenedicarbaldehyde [475,476].



SCHEME 103

A further extension of conjugation between the two 1,3-dithiol-2-ylidene heterocycles is attained by reaction of the mono(dimethylacetal) of fumaraldehyde with phosphoranes or phosphonate anions followed by conversion of the formed *trans*-aldehyde **142**. Wittig olefination of **142** with (1,3-dioxan-2-ylmethylene)tributylphosphorane yields trienic aldehydes **143**, which affords the TTF **144** with four conjugated double bonds by a further Wittig olefination with a phosphorane.

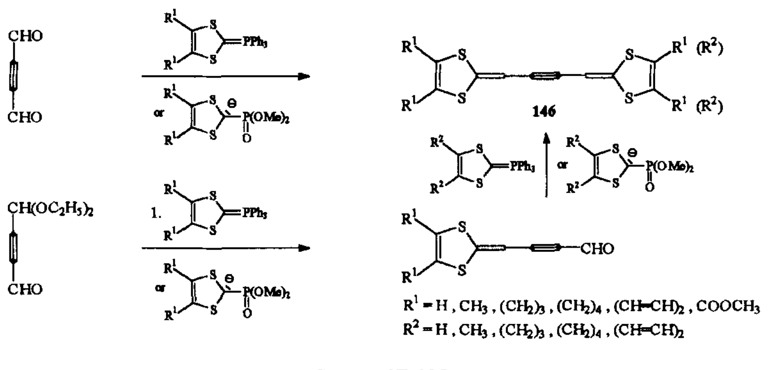
The TTF **145** with five conjugated double bonds ($n = 4$) is formed by a coupling of the aldehyde **142** [477]. Condensation of dialdehydes with 4,5-dicyano-1,3-dithiole-2-thione in the presence of triphenylphosphine provides, probably via a phosphorane, extended TTF **145** ($R^1 = CN$) with two ($n = 1$) to seven ($n = 6$) conjugated double bonds as spacers between the two 1,3-dithiole moieties. Under the same conditions the all-*trans*-2,6,11,15-tetramethylhexadeca-2,4,6,8,10,12,14-heptaene-1,16-dial forms a TTF with β-carotin-like structure. Aldehyde **143** [$R^1 = (CH{=}CH)_2$] reacts also with 4,5-dicyano-1,3-dithiole-2-thione and triphenylphosphine by forming of an unsymmetrical substituted TTF **144** [$R^1 = (CH{=}CH)_2$, $R^2 = CN$]. (Benzo-1,3-dithiol-2-ylidene) acetaldehyde or **142** [$R^1 = (CH{=}CH)_2$] forms under the same conditions with 4,5-dicyano-1,3-dithiole-2-thione and triphenylphosphine unsymmetrical substituted TTF [478]. These vinylogous TTF with great extension of the conjugation could have properties of 'molecular' wires.



SCHEME 104

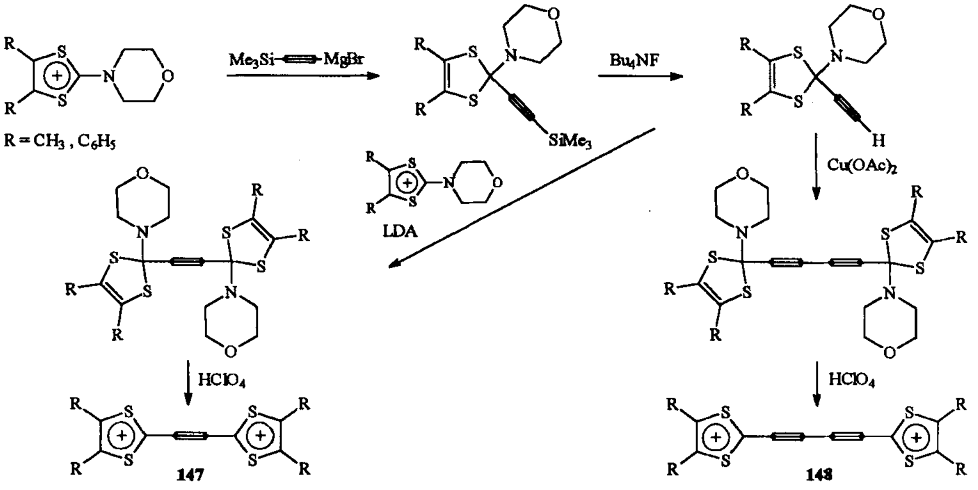
An extension of the π-system between the two 1,3-dithiol-2-ylidene moieties can also be achieved with olefinic and acetylenic bonds.

The Wittig or Wittig–Horner reaction of butynedial with phosphoranes or phosphonate anions, respectively, generates the symmetrical acetylenic analogues of TTF **146** [479,480]. From the mono(diethyl acetal) the unsymmetrical acetylenic analogues of TTF **146** can be obtained. The yields are increased when complexes of the dialdehyde or the mono(diethyl acetal) with dicobalthexacarbonyl are used as starting material instead of the corresponding free alkynes. The final decomplexation is achieved by treatment with trimethylamine oxide [481].



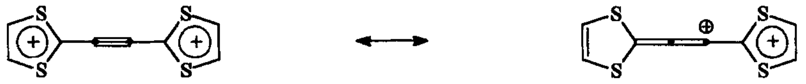
SCHEME 105

A cumulene skeleton has been inserted between the 1,3-dithioles in **147** and **148**. These TTF derivatives are formed by treatment of 2-morpholino-1,3-dithiolium salts with (trimethylsilyl)ethynyl magnesium bromide, followed by hydrolytic removal of the trimethylsilyl group. The dithiole thus obtained can be coupled with the starting 2-morpholino-1,3-dithiolium salts or dimerized in the presence of copper(II) acetate. Removal of the morpholino substituent by perchloric acid provides the cumulenic TTF [482]. So far only the dications **147** and **148** could be isolated in fairly good yields (70–90%). The neutral form is extremely unstable.



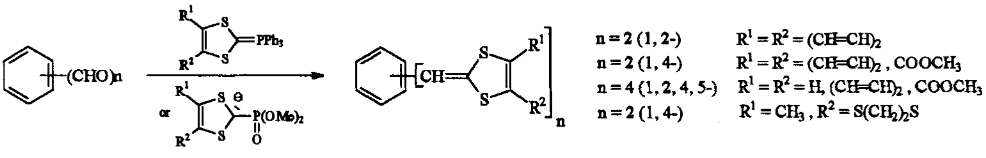
SCHEME 106

Both positive charges are more located in the two 1,3-dithiolium units than in the corresponding ethanediylidene units. Probably π-conjugation between the 1,3-dithiolium units is less effective through an acetylenic than through an olefinic bond.



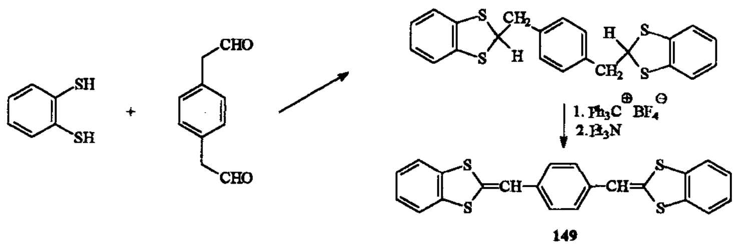
SCHEME 107

Via a Wittig or Wittig–Horner reaction, TTF derivatives are obtained with double bonds of olefinic and aromatic character between the two 1,3-dithiol-2-ylidene moieties in yields of 40–90% [483–486].



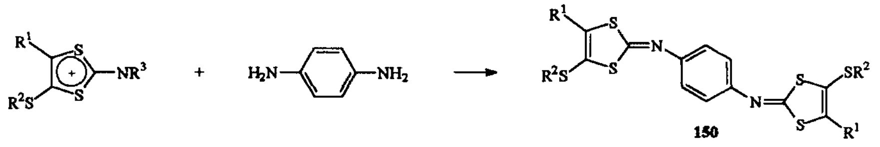
SCHEME 108

The 1,4-derivative **149** with $n = 2$ [$R = (CH{=}CH)_2$] is also formed by reaction of benzene-1,2-dithiole with 1,4-phenylene-diacetaldehyde and then subsequent hydride abstraction with trityl tetrafluoroborate and deprotonation with triethylamine [464].



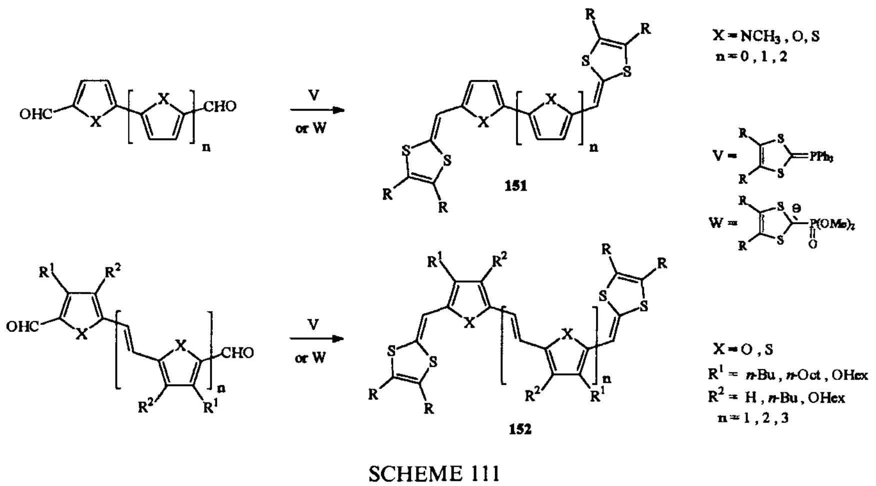
SCHEME 109

Treatment of 1,4-phenylenediamine with 2 molar equivalents of 2-amino-1,3-dithiolium salts yields *N*,*N*′-bis(1,3-dithiol-2-ylidene)-benzene-1,4-diamines **150** in the *trans* configuration. If the two sulfur atoms on R^2 are connected by a bridge [$(CH_2)_{10}$ or $(CH_2)_{12}$] the *cis* configuration is forced. Substitution of the CH linking group in 1,3-dithiol-2-ylidene compounds for an N group decreases significantly the donor properties of **150** [487,488].



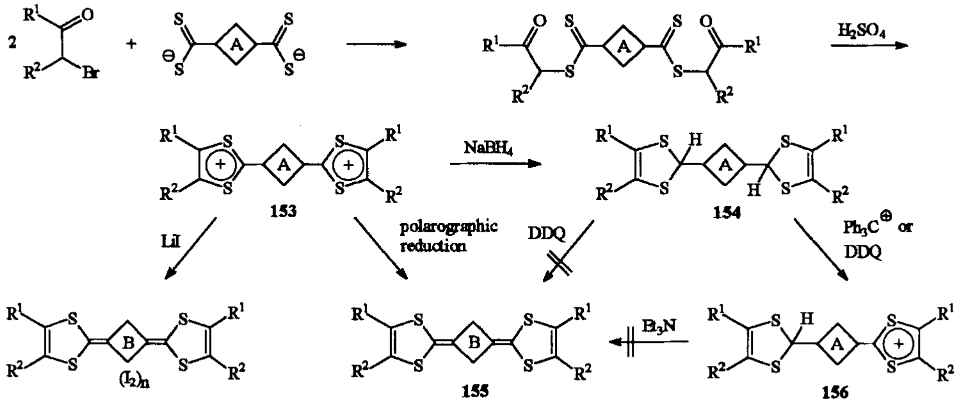
SCHEME 110

Conjugated TTF derivatives **151** with incorporated five-membered heterocycles are synthesized by Wittig or Wittig–Horner reaction of the corresponding heterocyclic dicarbaldehyde with phosphoranes or phosphonate anions, respectively [450,489–491]. In the same way oligothiophenes or oligofuranes **152**, incorporation of double bonds into the conjugated spacer, end-capped with 1,3-dithiol-2-ylidene moieties are formed. A better solubility of **152** is accomplished by substitution of alkyl [492–499] or alkoxy [500] chains.



SCHEME 111

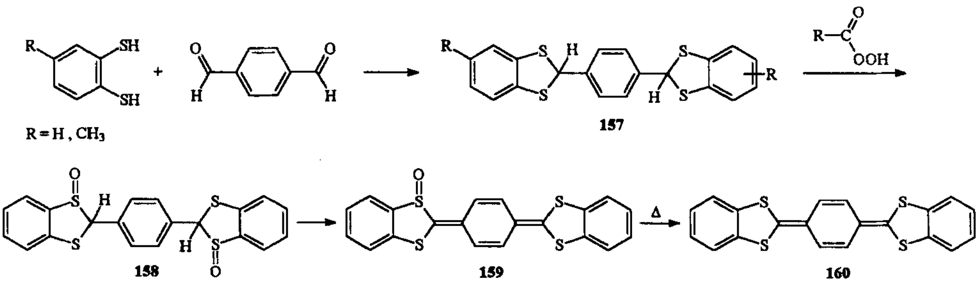
The 1,3-dithiolylidene units have also been connected by a 1,4-benzoquinoid system, but these compounds are rather unstable. The cyclization of the bis(dithioesters) with concentrated sulfuric acid provides the appropriate bis(1,3-dithiolium) salts **153** [501–509]. Many efforts reducing the dications **153** to the 1,4-benzoquinoid derivatives **155** were unsuccessful. As well by the dehydrogenation of **154** with DDQ as by the deprotonation of **156** with triethylamine the desired **155** could not be isolated [504–506]. With lithium iodide the dication **153** (A = 1,4-phenylene [474], 2,6-naphthalenediyl [476], 1,4-naphthalenediyl [505]) could be converted into a stable iodine complex. With DDQ or Li^+ $TCNQ^-$ the dications **151** form CT complexes with different composition [501,504,505]. Only in the cyclic voltammetry of the dications **153** is a reversible reduction to the neutral species **155** observed [505–507].



$R^1 = H, CH_3$ $R^2 = CH_3, C_6H_5$
A = 1,3-phenylene, 1,4-phenylene, biphenyl-4,4'-diyl, 1,4-naphthalenediyl, 2,6-naphthalenediyl, 9,10-anthracenediyl, 2,5-thienediyl

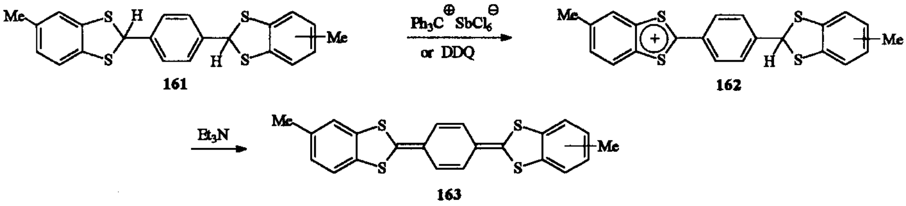
SCHEME 112

Benzo-annelated derivatives are formed by reaction of the corresponding 1,2-dimercapto compounds with terephthaldehyde. The unsubstituted derivative **157** (R = H) could not be dehydrogenated with chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [510,511]. Instead an unusual method is used. The dihydro compound **157** is oxidized with 1,3-chloroperbenzoic acid to the disulfoxide **158**, converted to the monosulfoxide **159** with diazabicyclononene and pyridine, the pyrolysis of which gives cyclohexa-2,5-diene-1,4-diylidenebis-1,3-benzodithiole **160** [510,511].



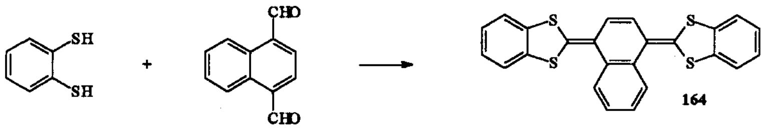
SCHEME 113

The dimethyl derivative **163** could be synthesized by treatment of the corresponding dihydro compound **161** with trityl hexachloroantimonate or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to form the monocation **162**, followed by deprotonation with triethylamine [512].



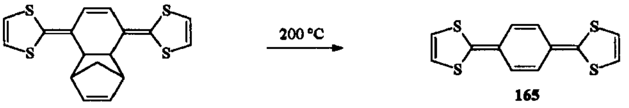
SCHEME 114

Both the unsubstituted and the dimethyl derivative **160** and **163**, respectively, are slightly air sensitive and decompose. In the same way the 1,4-naphthoquinoid compound **164** is formed [513].



SCHEME 115

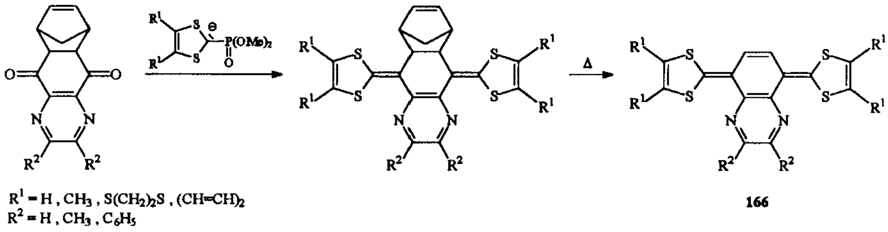
For the unsubstituted compound **155** ($R^1 = R^2 = H$, A = 1,4-phenylene) no details have been reported [514]. Somewhat later the unsubstituted quinodimethane analogue of TTF **165** could be prepared by a retro-Diels–Alder reaction of the corresponding cyclopentadiene adduct in 54% yield [515].



SCHEME 116

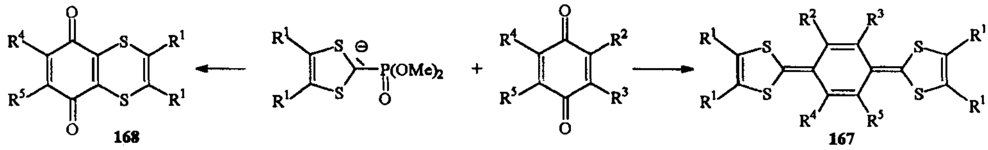
Pyrazine fused derivatives **166** [516–518] or thiadiazole and selenadiazole fused derivatives [519–523] are quantitatively obtained by this retro-Diels–Alder reaction of cyclopentadiene adducts.

Also other benzo- and naphtho-condensed quinodimethane analogues of TTF can be obtained by this retro-Diels–Alder reaction [515,518,524].



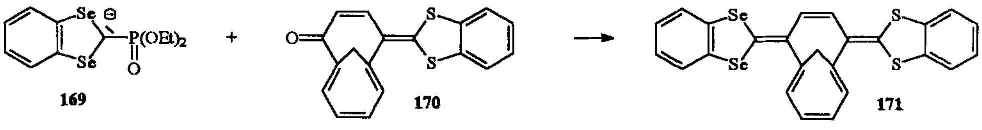
SCHEME 117

Quinodimethane analogues **167** of TTF have been synthesized by Wittig or Wittig–Horner reaction of quinones with phosphoranes or phosphonate anions, respectively. A number of annelated or heterocyclic fused quinoid structures have also been prepared in this way [251,505,518,519,523–541]. In the case of chlorine substituted quinones ($R^2 = R^3 = Cl$) the reaction did not lead to the expected 1,4-quinodimethane derivatives **167**, but afforded the novel 1,4-dithiin-fused quinones **168** [542].



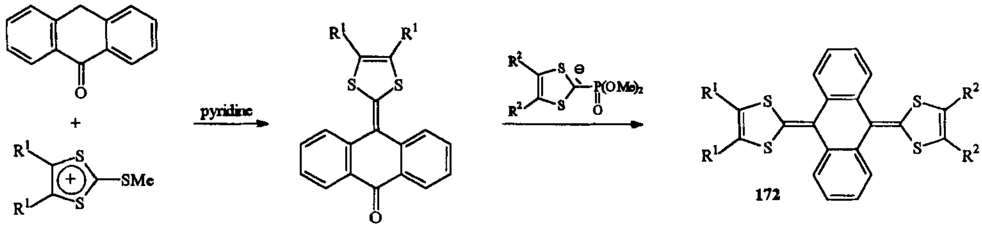
SCHEME 118

The Wittig–Horner reaction is also successful in the case of treatment of the (1,3-diselenol-2-yl)phosphonate anion **169** with the ketone **170** and provides, in quantitative yield, the vinylogous DTDSF **171** [543].



SCHEME 119

Asymmetrically substituted quinoid analogues of TTF **172** have been obtained (yield 55–70%) by treatment of 2-(alkylthio)-1,3-dithiolium salts with anthrone under basic conditions, followed by Wittig–Horner reaction with phosphonate anions [505,539,544–546].



SCHEME 120

Use of a 1,3-thiaselenolephosphonate anion as a starting material afforded trithiaselenafulvalenes [544].

Vinylogous, cumulenic, acetylenic, quinoid TTF and TSF and their data are summarized in Table B6.

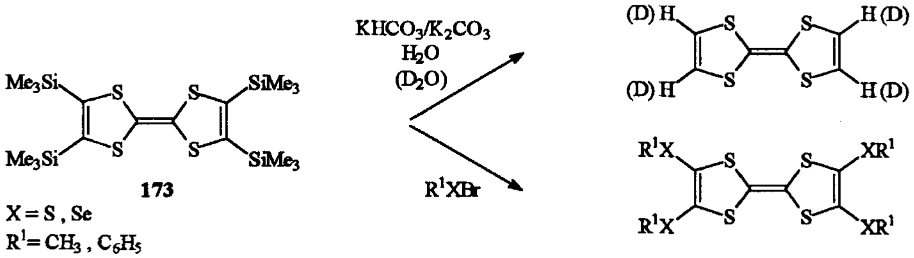
7. PROPERTIES OF TETRACHALCOGENAFULVALENES

7.1. Reactions of Tetrathia- and Tetraselenafulvalenes

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.

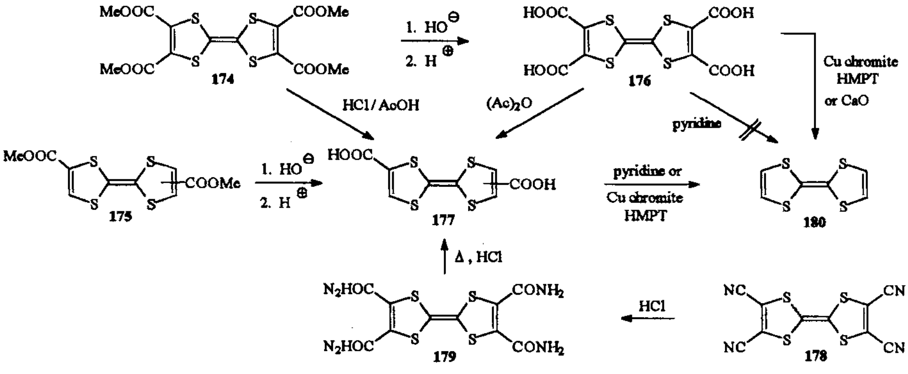
In ethanol/tetrahydrofuran (1 : 1) at room temperature with an aqueous buffer containing potassium carbonate and potassium hydrogen carbonate the trimethylsilyl groups of tetrakis(trimethylsilyl)tetrathiafulvalene **173** [272] or tetrakis[(trimethylsilyl)ethynyl]tetrathiafulvalene [547] are readily replaced by hydrogen. Treatment of 4,5′-bis[(trimethylsilyl)ethynyl]-5,4′-diphenyltetrathiafulvalene with 1 M aqueous KOH in ether/methanol easily generates the 4,5′-diethynyl-5,4′-diphenyltetrathiafulvalene [548].

Deuterated solvents (D_2O, EtOD) under the same conditions afford deuterated tetrathiafulvalene. With sulfenyl or selenyl bromides the corresponding tetrakis(organylthio)- or tetrakis(organylseleno)tetrathiafulvalenes are obtained [272].



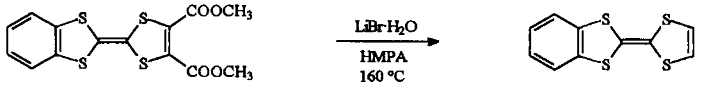
SCHEME 121

The tetrathiafulvalene tetraester **174** and the diester **175** can be hydrolysed in aqueous or ethanolic alkaline solution [116,199,200,273] as well as in half-concentrated hydrochloric acid/glacial acetic acid [182] to the corresponding tetraacid **176** or diacid **177**, respectively, where the hydrolysis is accompanied by decarboxylation under acidic conditions. Hydrolysis of tetracyanotetrathiafulvalene **178** in concentrated hydrochloric acid at room temperature gives tetrathiafulvalene tetracarboxamide **179**. Hydrolysis with reflux does not provide the amide **179**, but generates the diacid **177** by simultaneous decarboxylation [200]. The diacid **177** is also formed upon heating of the tetraacid **176** in acetic anhydride [200]. The diacid **177** decarboxylates in pyridine at 250°C in a sealed tube to give the parent tetrathiafulvalene **180** [116,200]. Under the same conditions the tetraacid **176** does not decarboxylate [200]. An alkyl and alkylthio-substituted TTF acid decarboxylates by refluxing in pyridine [259]. The decarboxylation of the diacid **177** as well as of the tetraacid **176** in hexamethylphosphoramide at 150°C in the presence of copper chromite gives the parent tetrathiafulvalene **180**. Also copper(II)sulfate or copper powder in quinoline induces the decarboxylation of acid derivatives [549]. The tetraacid **176** can be decarboxylated by heating at 300°C in the presence of calcium oxide [273].



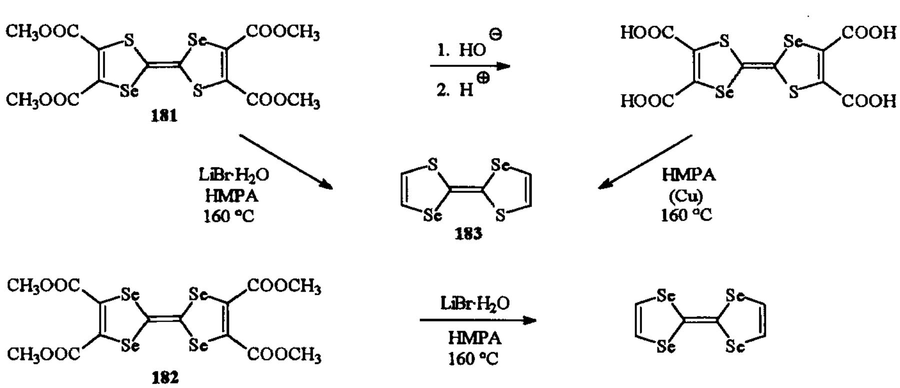
SCHEME 122

Hydrolysis and decarboxylation can be performed in one step by treatment of the corresponding methyl ester with lithium bromide monohydrate in hexamethylphosphoramide [208,240].



SCHEME 123

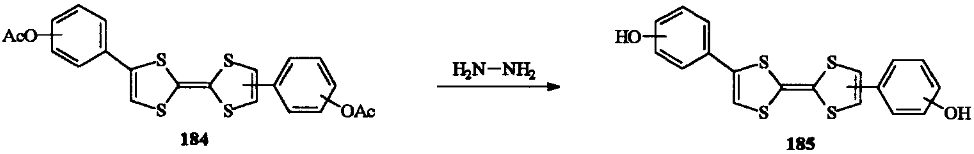
Under the same conditions the *sym*-dithiadiselenafulvalene **181** [382] and tetraselenafulvalene ester **182** [550] also decarbomethoxylate. The *sym*-dithiadiselenafulvalene **183** is also formed by hydrolysis of *sym*-dithiadiselenafulvalene tetracarboxylic acid tetraester **181** in alkaline solution, followed by decarboxylation in hexamethylphosphoramide in the presence of copper bronze [382,389].



SCHEME 124

For the hydrolysis of the substituted aryltetrathiafulvalenes **184** hydrazine in methanol is a convenient reagent [199,551].

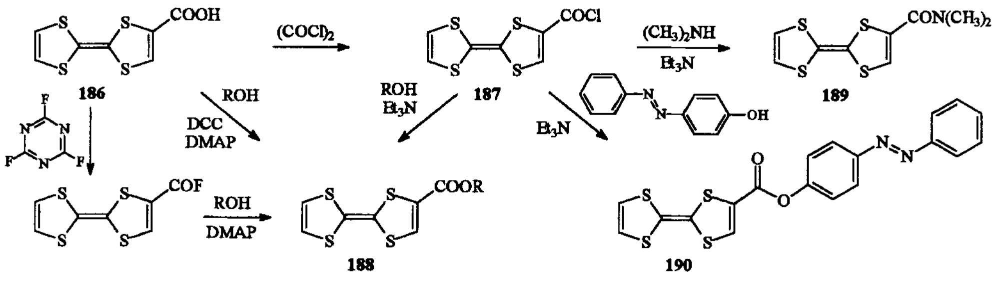
After treatment with long-chain acid chlorides in pyridine the 4,4′(5′)-bis(4-hydroxyphenyl)tetrathiafulvalene **185** constitutes TTF derivatives with liquid crystal properties [552,553].



SCHEME 125

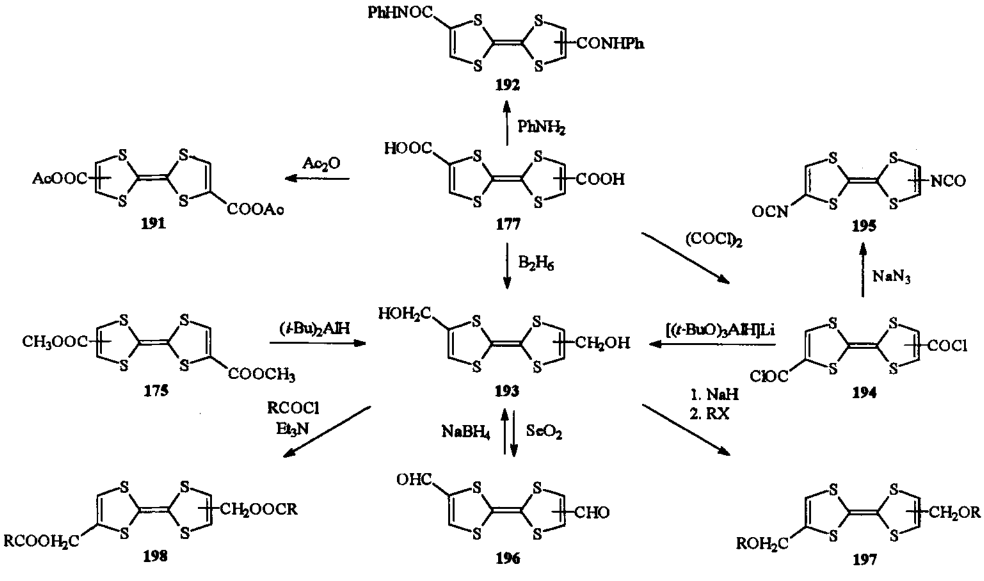
Esterification of tetrakis(hydroxyalkylthio)tetrathiafulvalene with 4-decyloxybenzoic acid was not successful, even under a variety of reaction conditions. However, tetrasubstituted TTF which bear promesogenic units such as 4-decyloxybenzoyl or 3,4,5-tris(decyloxy)benzoyl groups, the latter TTF showing mesogenic behaviour, are formed by reaction of dicobaltoctacarbonyl with the corresponding 1,3-dithiole-2-thione [220].

The carboxylic acid group in tetrathiafulvalene carboxylic acid **186** can be converted into other acid derivatives. With oxalyl chloride in dichloromethane [554] or benzene/acetonitrile [555] the acid chloride **187** or in tetrahydrofuran the ethylenedithio TTF acid chloride [556] is formed. The reactive **187** furnishes with alcohols [557] or amines [331] in the presence of triethylamine the corresponding esters **188** or amides **189**, respectively. With the azobenzene derivative, **190** is formed undergoing *trans–cis* isomerization of the azobenzene substituent upon photolysis. Semiconducting LB films of **190** are assembled without the need of added fatty acid [558]. The tetrathiafulvalene carboxylic acid **186** yields by the reaction with alcohols in the presence of dicyclohexylcarbodiimide (DCC) [559,560] or DCC and 4-*N*,*N*-dimethylaminopyridine (DMAP) the esters directly [213,561]. Under mild conditions the reaction of the TTF acid **186** provides with cyanuric fluoride and pyridine in dichloromethane the stable acid fluoride, which affords by treatment with alcohols and DMAP or amines the corresponding esters or amides in high yields, respectively [562,563].



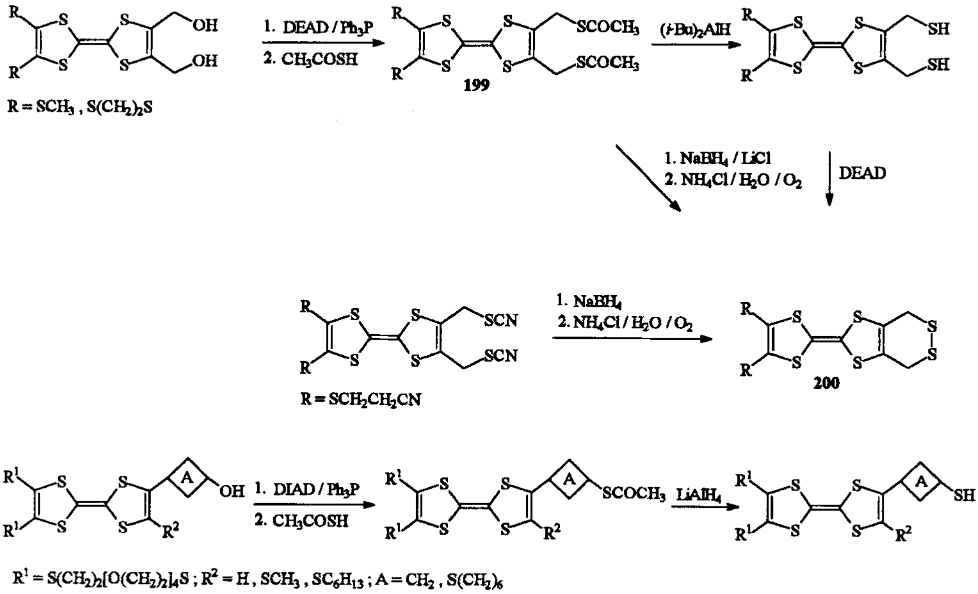
SCHEME 126

Also the tetrathiafulvalene diacid **177** can be transformed to various other acid derivatives. With acetic anhydride in tetrahydrofuran the bis-anhydride **191** is formed [199], with aniline in *N*,*N*-dimethylformamide at 70°C, with diphenyl phosphite/pyridine as dehydrating reagent, the bis-anilide **192** [199], and with diborane in diglyme the bis(hydroxymethyl)-tetrathiafulvalene **193** is obtained [199]. The tetrathiafulvalenedicarbonyl dichloride **194**, formed by the reaction of the diacid with oxalyl chloride, yields, with activated sodium azide in benzene or toluene, in a Curtius reaction the corresponding isocyanate **195** [554,555]. Tetrathiafulvalenedicarbonyl dichloride **194** is reduced with lithium tri-*t*-butoxyaluminium hydride in tetrahydrofuran to bis(hydroxymethyl)-tetrathiafulvalenes **193** [554]. Both ester groups in the TTF **175** are reduced with diisobutylaluminium hydride in tetrahydrofuran at – 10°C to the alcohol groups [206]. Unsubstituted [564] or substituted [152,213,293,565] monoesters are also reduced with diisobutylaluminium hydride in dichloromethane at lower temperatures (– 50°C to – 80°C) to the corresponding monoalcohols. A diester to the dialcohol is reduced with sodium borohydride in the presence of zinc chloride in refluxing tetrahydrofuran [213,565,566] or dichloromethane [152]. The ester groups in tetrakis(methoxycarbonyl)tetrathiafulvalene are selectively reduced with sodium borohydride activated by lithium chloride in tetrahydrofuran–methanol (4 : 1) at 0°C. Under different reaction conditions (differing ratio of TTF derivative : $NaBH_4$: LiCl) different amounts of the mono-, di-, tri-, and tetraalcohols are formed which are separated by column chromatography [567,568]. The aldehyde [564,565,569] and the keto [341] group can be reduced by use of sodium borohydride to afford alcohols and racemic alcohols, respectively. The dialcohol **193** or monoalcohols are oxidized with selenium dioxide in refluxing dioxane to the corresponding aldehyde **196** isolated as a *cis–trans* mixture, confirmed by ^1H and ^{13}C NMR measurements [206,570]. The ethylenediselenotetrathiafulvalene dialcohol is also oxidized with manganese dioxide in dichloromethane at room temperature. The oxidation of the ethylenediselenotetrathiafulvalene monoalcohol with selenium dioxide or maganese dioxide was not successful [152]. But mono(crown)tetrathiafulvalene monoalcohol can be oxidized with selenium dioxide to the corresponding aldehyde [293]. Dialcohol **193** provides with sodium hydride, followed by alkylating agents, ethers **197** and with acyl halides in the presence of triethylamine esters **198** [571,572]. Esters are also formed by reaction of TTF dialcohols with acids in dichloromethane in the presence of DCC and DMAP [568].



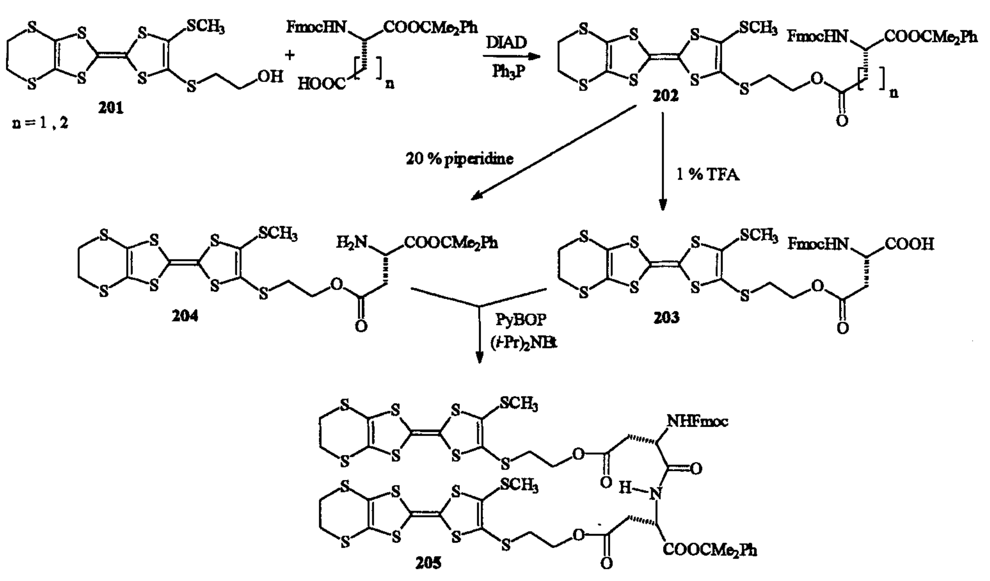
SCHEME 127

Mono- or dihydroxymethyl TTF derivatives are converted in mono- or bis(thioesters) using Volante's modification of the Mitsunobo reaction. The corresponding TTF derivatives react with the diisopropylazodicarboxylate (DIAD) or diethylazodicarboxylate (DEAD)/triphenylphosphin complex in tetrahydrofuran and subsequent *in situ* displacement of the resulting leaving group with thioacetic acid yields the thioesters **199**. The reduction of the thioesters with lithium aluminium hydride in ether [213] or the bis(thioesters) with diisobutylaluminium hydride in dichloromethane [566] affords the corresponding thiols or dithiols, respectively. Oxidation of the dithiols with DEAD forms the unsymmetrical *S*-position isomers **200** of bis(ethylenedithio)tetrathiafulvalene. The synthesis is also successful in a one-pot reaction by cleaving the thioester groups with sodium borohydride in the presence of lithium chloride [566] or thiocyanato groups with sodium borohydride [212], followed by treatment with ammonium chloride solution and oxidation by air. The symmetrical *S*-position isomer **200** (R=CH_2S–SCH_2) of BEDT-TTF is formed by cleavage of the corresponding tetra(thioester) with sodium methoxide and oxidation by air [573].



SCHEME 128

The readily prepared hydroxyethylthiotetrathiafulvalene **201** is linked with protected amino acids (Fmoc = 9-fluorenyl-methoxycarbonyl) under Mitsunobo conditions (DIAD) achieving the TTF-derived amino acids **202**. After selective acid deprotection (1% TFA in dichloromethane) or amino deprotection (20% piperidine in THF) the corresponding TTF-acid **203** and TTF-amine **204** are formed ($n = 1$), which are coupled (PyBOP = tris(pyrrolidinyl)benzotriazolyloxyphosphonium hexafluorophosphate) to a dipeptide **205**. Successive acid deprotection and conversion with the TTF-amine provides tri- and tetrapeptides [574].



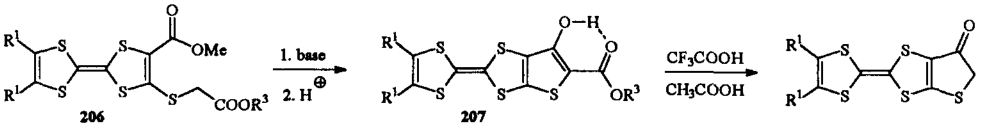
SCHEME 129

In successive esterification/deprotection reactions of the monoalcohol hydroxymethyltetrathiafulvalene with 5-(*t*-butyl-dimethylsiloxy)isophthalic acid chloride/tetrabutylammonium fluoride and subsequent reaction with 1,3,5-benzene-tricarboxylic acid chloride [211,575] or esterification reaction of diacid chlorides with 5-hydroxyisophthalic esters, bearing the TTF framework [211,576], TTF dendrimers with 3, 4, 6, 8 or 12 TTF moieties at the periphery of the molecule could be synthesized. Analogously, a substituted 2-(hydroxymethyl)-1,3-propanediyldithiotetrathiafulvalene yields dendrimers with 2 or 6 TTF moieties, but their stability was low [211]. Esterification of benzoylchloride derivatives, bearing TTF moieties, with phenol derivatives, bearing the anthraquinone framework, leads to the formation of polyester dendrimers containing TTF (4, 8) as well as anthraquinone units (2, 4) in a molecule [577].

In an iterative procedure TTF thiolate anions (generated by the *in situ* deprotection of their cyanoethyl derivatives) reacted with benzylic chloride derivatives or glycol derivatives to yield TTF dendrimers with 13 [578] or 21 [579] TTF units, respectively. The six-fold reaction of a substituted TTF thiolate anion with hexakis(bromomethyl)benzene affords the corresponding dendrimer with 6 TTF units [580]. 1,3,5-Tris (bromomethyl)benzene, hexakis(bromomethyl)benzene or tetrakis(4-chloromethylbenzylthio) TTF react with TTF thiolate anions of TTF trimers or heptamers where the TTF units are connected by glycol chains and provide dendrimers up to 18 TTF units [581].

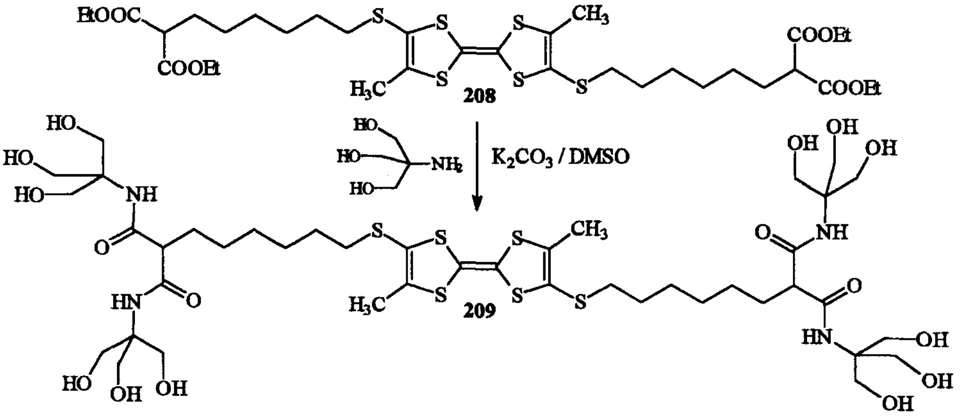
Dendrimers with TTF moieties as redox-active substituents readily yield multiply-charged species in multi-electron processes and can show interesting properties (e.g. as electron-transfer catalysts, electronic and photo-optical materials, organic magnets) [56].

Reaction of base (sodium methoxide or potassium *t*-butoxide) with a TTF derivative **206**, substituted by a methoxycarbonylmethylthio group and a neighbouring methoxycarbonyl group, yields by cyclization a [2,3-d]thieno-condensed TTF **207** [582], which is decarboxylated by heating with a mixture of trifluoroacetic acid/acetic acid [583].



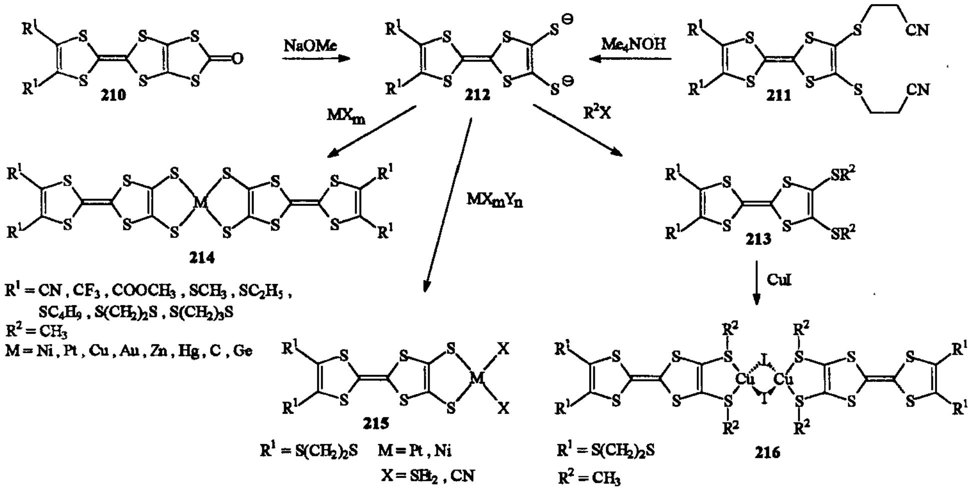
SCHEME 130

Amidation of a long chain substituted TTF ester **208** with tris(hydroxymethyl)aminomethane provides a new TTF derivative **209**, which forms a gel. Structure investigations prove string-like superstructures with lengths of the order of microns and diameters ranging from about 30 to several hundred nanometers. In connection with the conductivity properties of the TTF moiety, such a compound could be a candidate for 'molecular' wires [584].



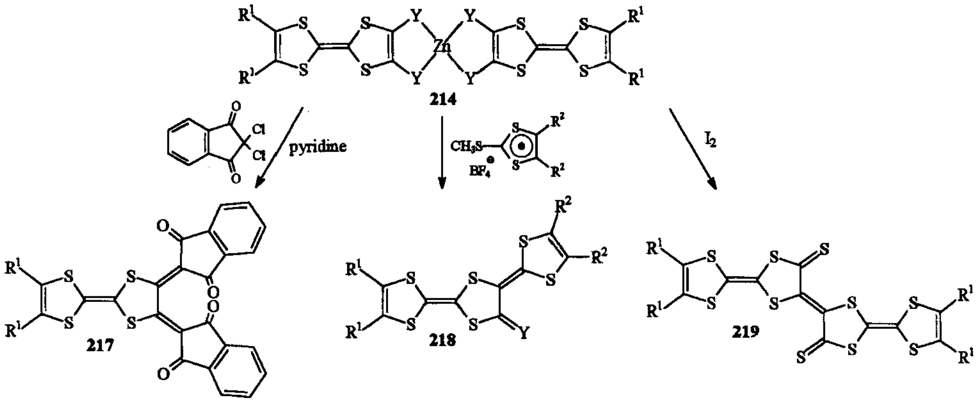
SCHEME 131

1,3-Dithiol-2-ono-annelated TTF **210** are degraded by strong bases like sodium methoxide or methyllithium [224,585,586]. The 4,5-bis(2-cyanoethylthio)tetrathiafulvalene **211** can be deprotected in dichloromethane or tetrahydrofuran by using tetramethylammonium hydroxide as the base [587–589]. The dithiolate salts **212** so formed can be converted with alkylating agents into different substituted tetrathiafulvalenes **213** [586] and with transition metal salts to the corresponding metal dithiolene complexes **214** [586–594] or asymmetrical complexes **215** [595,596]. The 4,5-di(methylthio)-substituted TTF **213** forms with copper(I)iodide in acetonitrile the coordination dimer **216** as an extended donor of the D-σ-D type [597].



SCHEME 132

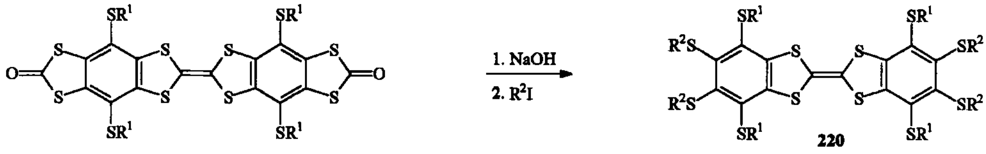
Tetrathiafulvalenylylidenes are formed by reaction of zinc dithiolene complexes **214** with electrophiles [598,599] or oxidation with iodine [600]. These compounds exhibit in dichloromethane absorptions in the visible to the near-infrared region (**217**: $\lambda_{max} = 861$ nm, **218**: $\lambda_{max} = 589$–623 nm, **219**: $\lambda_{max} = 1\,118$ nm).



SCHEME 133

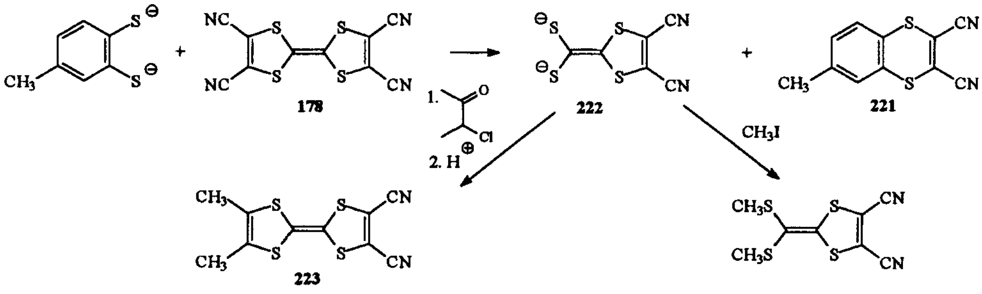
Bis(1,3-dithiol-2-ono)tetrathiafulvalene [124,129,590,601,602] and tetrakis(benzoylthio)tetrathiafulvalene [603] are also cleaved by strong bases. The air-sensitive tetrathiolate salt thus obtained affords, upon addition of alkylating agents, the corresponding TTF [124,601,604] and with transition metal salts the polymeric dithiolene complexes [129,590,602]. When only two equivalents of base are used and subsequently treated with methyl iodide, the half-opened di(methylthio) derivative is formed [601].

Sodium hydroxide in dimethylsulfoxide hydrolyses the 1,3-dithiol-2-one system also in the benzo-annelated TTF **220** [605,606]. The tetrathiolate formed can be alkylated with alkyl iodides.



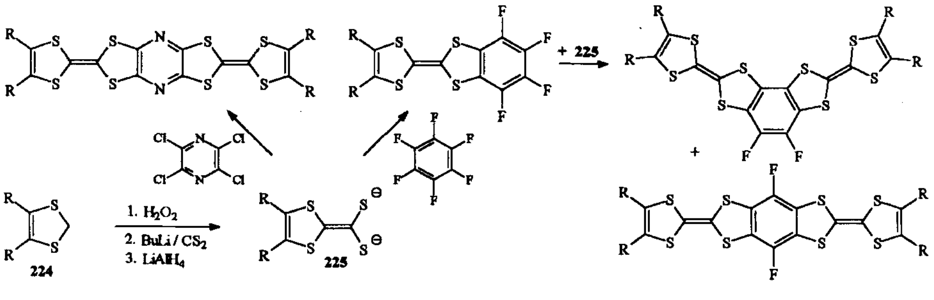
SCHEME 134

The nucleophilic attack of the salt of 3,4-toluenedithiole upon tetracyanotetrathiafulvalene **178** provides 2,3-dicyano-5,6-toluo-1,4-dithiene **221** and the air-sensitive geminal dithiolate intermediate **222**, which can be converted with methyl iodide or 3-chloro-2-butanone and subsequently with concentrated sulfuric acid into a new tetrathiafulvalene derivative **223**. Also alkane-, arene-, acylthiols, -selenol and -tellurol salts react with tetracyanotetrathiafulvalene **178** in analogous manner to give the geminal dithiolate intermediate **222**. Tetracyanotetraselenafulvalene reacts in a similar fashion [607].



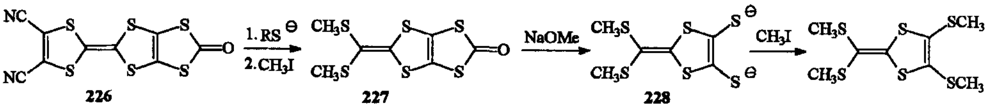
SCHEME 135

Substituted geminal dithiolates **225** as intermediates can be prepared by oxidation of the corresponding dithioles **224** [608] with hydrogen peroxide, forming the monosulfoxides, which are further converted with butyl lithium and carbon disulfide into the monosulfoxides of the dithiolates. Subsequent reduction with lithium aluminium hydride affords the dithiolates **225**. The dithiolates can be used as a synthon for preparing π-extended TTF derivatives in nucleophilic aromatic substitution reactions [609].



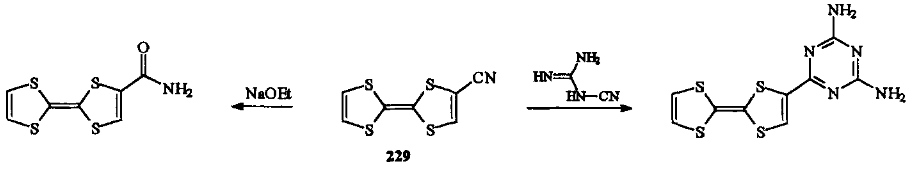
SCHEME 136

The reaction of the asymmetrically substituted tetrathiafulvalene **226** with thiolates leads to attack preferentially at the cyano substituted double bond. After alkylation with methyl iodide **227** is formed, which can be cleaved at the bithiocarbonate group with a stronger base (NaOMe, MeLi) to give a 1,2-dithiolate intermediate **228**, which is then alkylated [607].



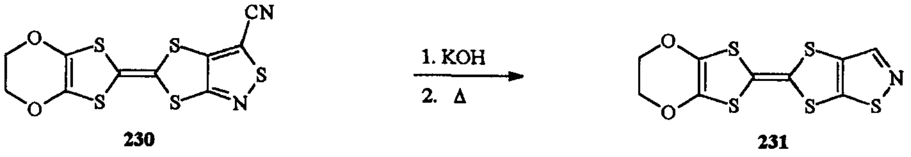
SCHEME 137

Cyanotetrathiafulvalene **229** can be hydrolysed with an excess of sodium ethoxide in ethanol forming amido TTF. The reaction of **229** with dicyandiamide under basic conditions yields a diaminotriazine derivative (66%) [610].



SCHEME 138

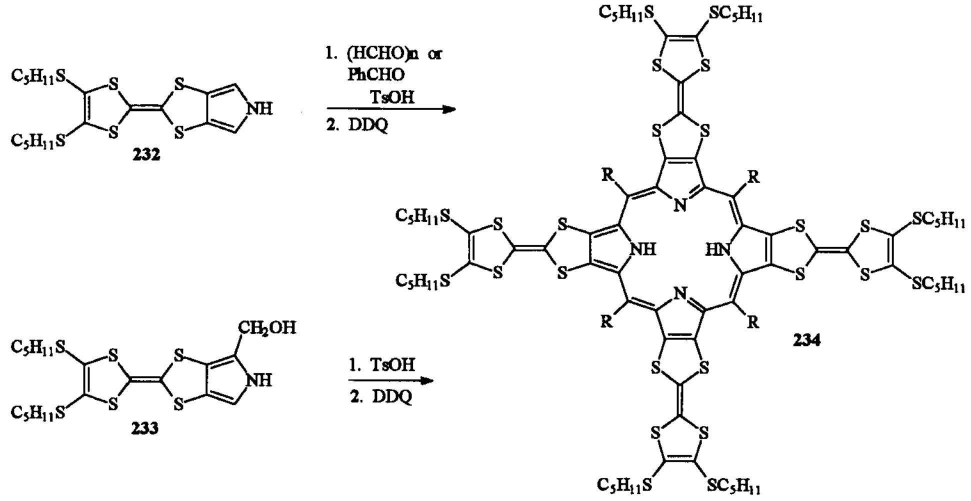
Refluxing of the thiazoloethylenedioxotetrathiafulvalene **230** in alkaline solution, followed by heating of the acid in DMF with decarboxylation and simultaneous rearrangement, provides the isothiazoloethylenedioxotetrathiafulvalene **231** [611].



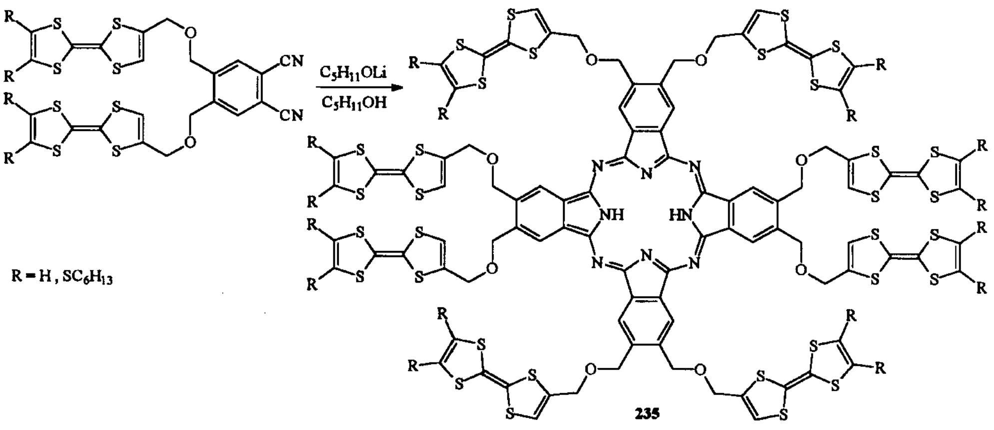
SCHEME 139

The porphyrine core with four directly annelated TTF moieties is synthesized by two synthetic routes. The porphyrinogen is formed either by reaction of the pyrrolo-TTF **232** with paraformaldehyde or benzaldehyde and catalytic amounts of 4-toluenesulfonic acid (TsOH) in tetrahydrofuran at room temperature or by treatment of the alcohol **233** with 4-toluenesulfonic acid in ethanol at room temperature. Oxidation of the porphyrinogen with DDQ affords a mixture of the neutral porphyrin **234** and the radical cation (R = H, 4 : 1) [612].

Lithium pentoxide in pentanol at 140°C leads to tetramerization of dinitriles with attached tetrathiafulvalene derivatives to form the corresponding phthalocyanines **235** [613–615]. The fluorescence of the phthalocyanine **235** is quenched, probably by rapid intramolecular electron transfer between the phthalocyanine core and a peripheral TTF [614].



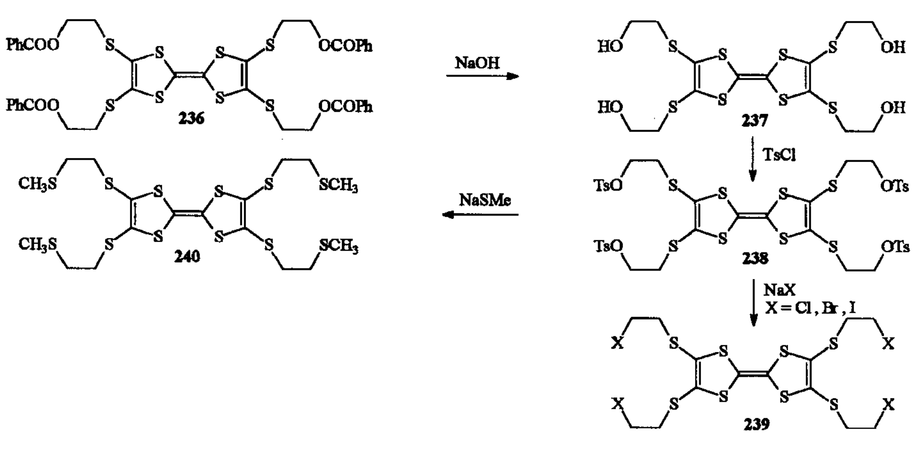
SCHEME 140



SCHEME 141

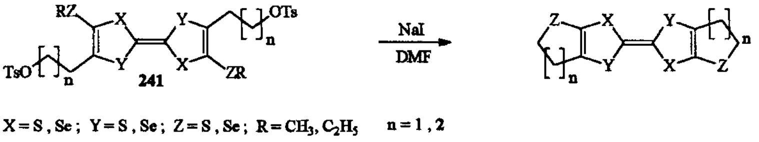
In esterification reactions the tetrathiafulvalene carboxylic acid is coupled to phthalocyanines [616].

Halides or tosyl chloride can also be used as nucleophilic or electrophilic agents, respectively, so that substituents can be modified without conversion of the TTF moiety [617,618]. Hydrolysis of tetrakis(benzoyloxyethylthio)tetrathiafulvalene **236** takes place in alkaline solution to form tetrakis(hydroxyethylthio)tetrathiafulvalene **237**. This compound reacts with tosyl chloride to the corresponding tosylate **238**, which can be further converted with sodium halides and sodium methanethiolate into the tetrakis(haloethyl-thio)tetrathiafulvalene **239** and tetrakis(methylthioethylthio)tetrathiafulvalene **240**, respectively, in almost quantitative yield.



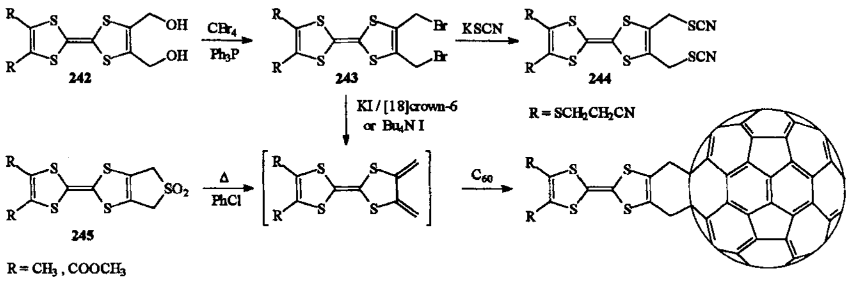
SCHEME 142

An outer five- or six-membered heterocycle is formed by heating of alkylchalcogeno-substituted DTDSF or TSF tosylates **241** or chlorides with sodium iodide in DMF. The tosyl group or chloride is substituted by iodide and concurrently a transalkylation reaction on the outer chalcogene atom of the resulting iodide occurred, affording the outer ring [113–115,218,419].



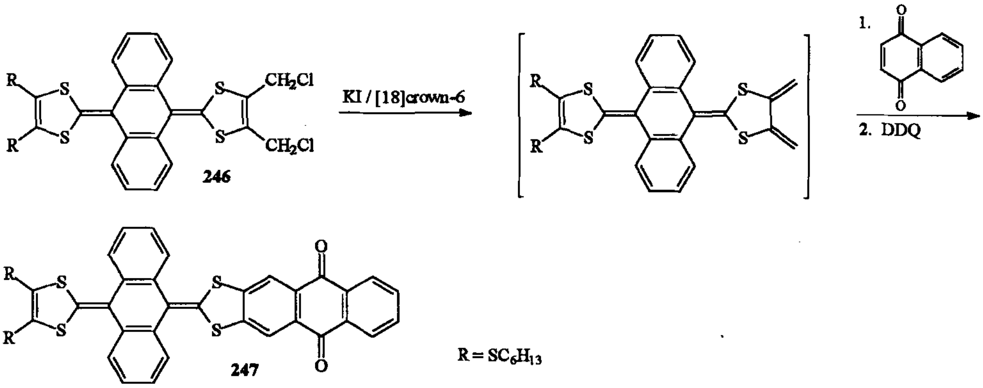
SCHEME 143

A direct conversion of the dialcohol **242** in the halo derivative **243** is successful by the reaction of **242** with carbon tetrabromide [619,620] in the presence of triphenyl phosphine [212,546]. **243** shows a high reactivity and provides quantitatively with potassium thiocyanate the corresponding TTF thiocyanato methyl derivative **244** [212] or can be used as a diene precursor in a [4 + 2] Diels–Alder cycloaddition with C_{60} [546,619–621]. The corresponding tetrakis(bromomethyl) TTF affords in the iodide-induced reduction of this TTF derivative and following Diels–Alder reaction with C_{60} the dumbbell triad C_{60}-TTF-C_{60} [622]. As a diene precursor for cycloaddition with C_{60} the TTF **245**, bearing a labile 3-sulfolene group, can be used [107,623].



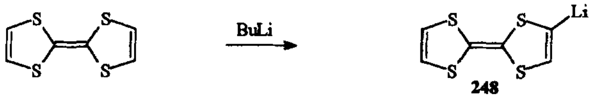
SCHEME 144

In the same way the bis(chloromethyl)-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivative **246** affords with KI/[18]crown-6 a diene, which yields in a cycloaddition to 1,4-naphthoquinone and subsequent oxidation with DDQ the aromatized TTF derivative **247** [45].



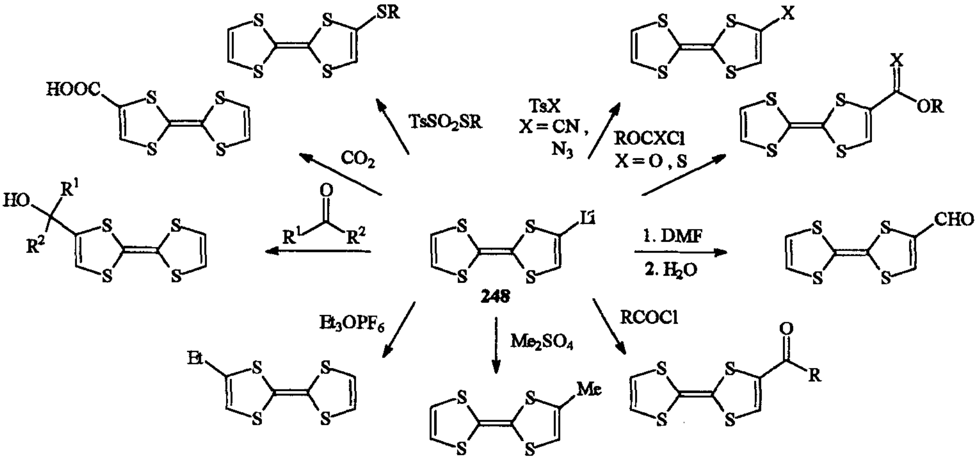
SCHEME 145

Metallation of TTF with different lithiation agents (LDA—lithium diisopropylamide, LiHMDS—lithium hexamethyldisilazane, PhLi, MeLi, BuLi) provides tetrathiafulvalenyllithium **248** as a reactive intermediate [368].



SCHEME 146

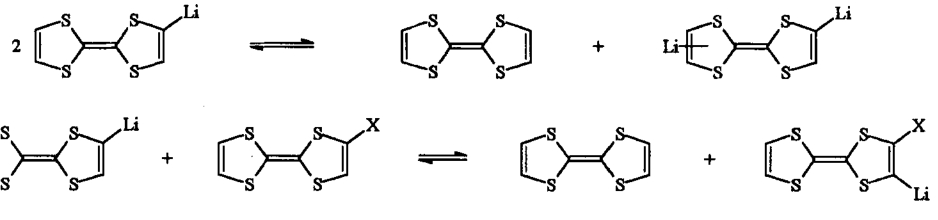
This key intermediate **248** can be converted with electrophiles to form monosubstituted TTF. This reaction constitutes a general method for the synthesis of a symmetrically substituted TTF [368,431,610,624–628].



SCHEME 147

In most cases the reaction of tetrathiafulvalenyllithium **248** with electrophiles leads to disubstituted derivatives as by-products. This is probably due to the tendency of tetrathiafulvalenyllithium to undergo disproportionation. Substituents on the TTF skeleton direct the second lithiation and hence the second substitution. Electron-donating substituents, such as lithium or methyl groups, decrease the acidity of the adjacent proton, and thereby direct substitution to the opposite ring.

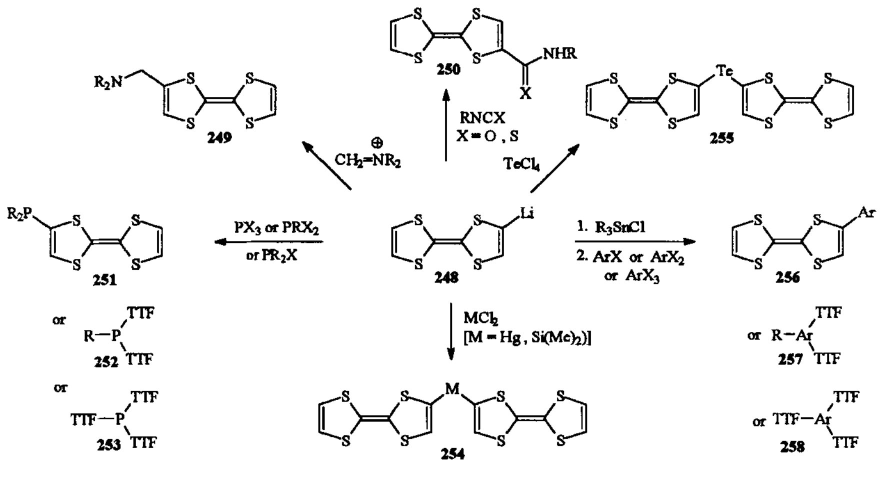
Halogens, formyl groups or acyl substituents as electron-withdrawing substituents increase the acidity of the adjacent proton and direct the second substitution to the same ring [368,610,627,629–634].



SCHEME 148

The first *N*,*N*-dialkylaminomethyl substituted TTF **249** were obtained in yields of 35–50% by reaction of tetrathiafulvalenyllithium **248** with Eschenmoser's salts [635]. The best yields were obtained with LDA as the metallation agent. Lithiation of TTF [625,636] or TTF derivatives [637] with LDA and subsequent treatment with isocyanates or isothiocyanates yields the amido- (besides 20% isocyanato-TTF [627]) or thioamido-TTF **250**.

The metallated TTF **248** provides with the halides PR_2X or PRX_2 or PR_3 the corresponding monomeric PR_2TTF **251**, the dimers $PR(TTF)_2$ **252** or the trimers $P(TTF)_3$ **253** [638–641]. Bridged dimeric TTF **254** can also be formed by reaction of main-group element halides with lithiated TTF **248** [639]. With $TeCl_4$ the monoanion yields only the dimer $Te(TTF)_2$ **255** [642,643]. After reaction of tetrathiafulvalenyllithium **248** with a trialkylstannyl chloride the corresponding trialkylstannyl derivative is formed. The corresponding mono-, bi-, or tritetrathiafulvalenes **256–258** can be prepared by palladium catalysed coupling of the trialkylstannyl derivative with mono-, di- or trihaloarenes [644–648]. Halomethanoannulenes [649], 1,1-dibromoethylenes [650] or iodothiophenes [651] can also be used.



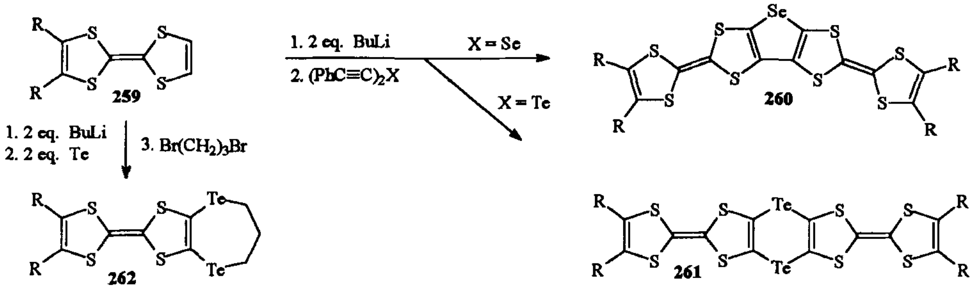
SCHEME 149

Tetrathiafulvalenyllithium **248** forms with zinc chloride the corresponding tetrathiafulvalenylzinc derivative, which affords with iodo TTF in the presence of $Pd(PPh_3)_4$ in a homo-coupling reaction bi- or tri- or tetratetrathiafulvalenes [652]. Iodo TTF can also be converted into bitetrathiafulvalenes by the Ullmann coupling (copper in refluxing DMF or copper(I)thiophene-2-carboxylate in *N*-methylpyrrolidone) [653].

In a similar manner the trimethylstannyltetraselenafulvalene is synthesized, which provides in a copper(II)- or palladium(II)-catalysed homo-coupling reaction bitetraselenafulvalene [654].

Lithiation of TTF with 2.5 equiv of LDA and subsequent reaction with trialkyl- or triphenylstannyl chloride gives the corresponding bis(trialkylstannyl)- or bis(triphenylstannyl)tetrathiafulvalenes, respectively [655].

Two TTF moieties can be linked to each other by a selenium atom or two tellurium atoms, if the 4,5-positions in the TTF derivative **259** are substituted. After lithiation with two equivalents of BuLi and reaction with bis(phenylethynyl) selenide or telluride the fused systems **260** or **261** containing a selenophene or a ditellurine ring, respectively, are formed [656–658]. The intermediate formed lithium ditellurolate can be converted also with 1,3-dibromopropane into the corresponding mono(propyleneditelluro) tetrathiafulvalene **262** [659,660].

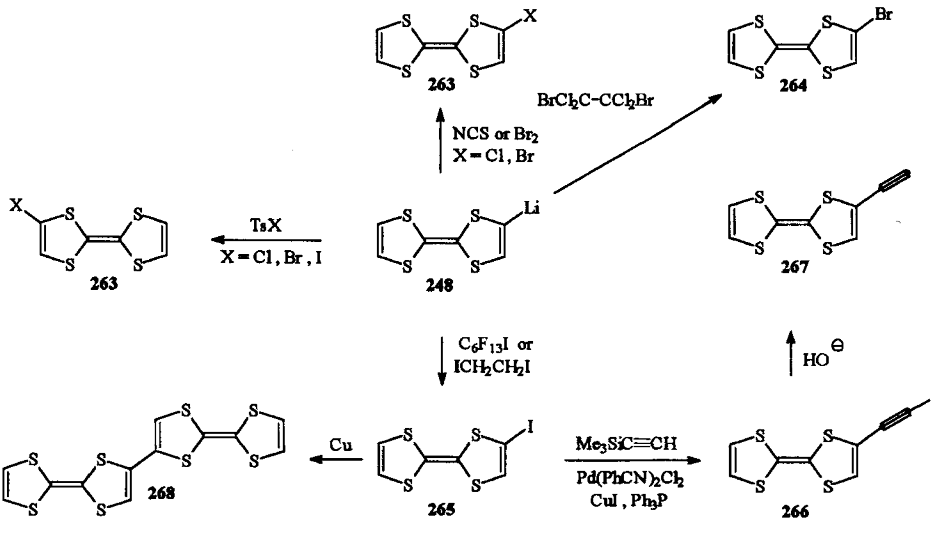


SCHEME 150

Halogenation of the lithiated species **248** (generated by LDA) with the appropriate 4-toluenesulfonyl halide affords the monohalogenated TTF derivatives **263** in good yields (35–50%) and the 4,5-dichloro- (4%) or 4,5-dibromo-tetrathiafulvalene (5%) as by-products [631]. The yield of bromotetrathiafulvalene **264** is decreased when 1,2-dibromo-tetrachloroethane is used as the halogenating agent. Beside the 4,5-dibromotetrathiafulvalene, also tri- and tetrabromo derivatives are formed. The yield of by-products depends on the kind of metallation agent [632].

The yield of **264** is also decreased (16%) if the bromination is carried out with *N*-bromosuccinimide, where 4,5-dibromotetrathiafulvalene (8%) is formed as by-product [661]. Using *N*-chlorosuccinimide or bromine as halogenating agents provides chloro- or bromotetrathiafulvalene **263** in moderate yields (11 and 34%, respectively). In both cases the corresponding 4,4′(5′)-dihalotetrathiafulvalenes are found as by-products [633], contrary to the halogenation with 4-toluene-sulfonyl halides or 1,2-dibromotetrachloroethane. Later it was found that the reaction of tetrathiafulvalenyllithium with *N*-chlorosuccinimide provides the 4,5-dichlorotetrathiafulvalene and not the 4,4′(5′)-dichlorotetrathiafulvalene [661].

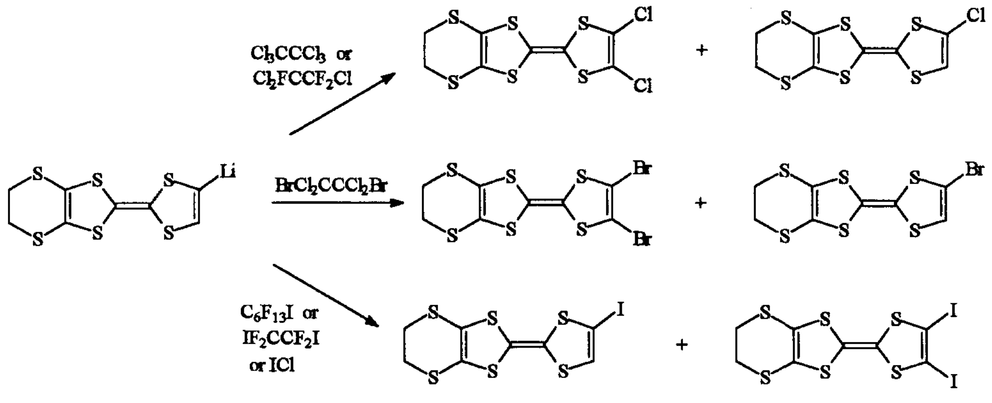
Monoiodotetrathiafulvalene **265** is prepared in good yields (70–78%) by treatment of TTF with LDA, followed by reaction with perfluorohexyl iodide or 1,2-diiodoethane [634,662]. 4-Iodotetrathiafulvalene reacts with trimethylsilylacetylene in the presence of $Pd(PhCN)_2Cl_2/CuI/Ph_3P/Et_3N$ as catalyst to afford 4-[(trimethylsilyl)ethynyl]tetrathiafulvalene **266** in 70% yield, which can be hydrolysed under alkaline conditions to produce 4-ethynyltetrathiafulvalene **267** [662]. In the same way the 4,4′(5′)-diphenyltetrathiafulvalene is converted via the 4,5′-diiodo-4′,5-diphenyltetrathiafulvalene and 4,5′-bis[(trimethylsilyl)ethynyl]-5,4′-diphenyltetrathiafulvalene into the 4,5′-diethynyl-4′,5-diphenyltetrathiafulvalene [548]. With copper powder in chlorobenzene at 130–140°C the 4-iodotetrathiafulvalene **265** provides a mixture of products where the TTF–TTF **268** can be separated after column chromatography [663]. Under the same condition in refluxing DMF the corresponding hexamethyldimer could be obtained. Better yields affords copper(I)thiophene-2-carboxylate as catalyst in *N*-methylpyrrolidinone [664]. The formation of **268** in a palladium-catalysed homocoupling of trialkylstannyltetrathiafulvalene with palladium chloride is reported, but these authors found a much higher melting point [644].



SCHEME 151

Monolithiated ethylenedithiotetrathiafulvalene can be halogenated with different halogenating reagents. With two equivalents of hexachloroethane or 1,2-dibromotetrachloroethane mainly the corresponding dihalides besides small amounts of the monohalides are formed. A better yield of the monochloride is obtained by use of 1,1,2-trichloro-1,2,2-trifluoroethane as chlorinating reagent. In contrast to chlorination and bromination, iodination with perfluorohexyl iodide or 1,2-diiodotetrafluoroethane [665] or iodine chloride [666,667] gives the monoiodide as the main product. Contrary to the synthesis of the iodoethylenedithiotetrathiafulvalene the main product of the iodination of the ethylenedithiotetraselenafulvalene with iodine chloride was the diiodoethylenedithiotetraselenafulvalene [667].

Monolithiated ethylenedioxytetrathiafulvalene provides with iodo-1,2-dichloro-1,2,2-trifluoroethane the corresponding monoiodide. The diiodoethylenedioxytetrathiafulvalene is formed by using two equivalents of LDA and quenching with perfluorohexyl iodide (3 equiv.) [668].



SCHEME 152

Reaction of 4,5-di(methylthio)tetrathiafulvalene with three equivalents of LDA and subsequent chlorination (hexachloroethane), bromination (1,2-dibromotetrachloroethane), or iodination (1,2-diiodotetrafluoroethane) produced mainly the dihalogenated TTF derivatives with small amounts of the monohalogenated TTF derivatives [669].

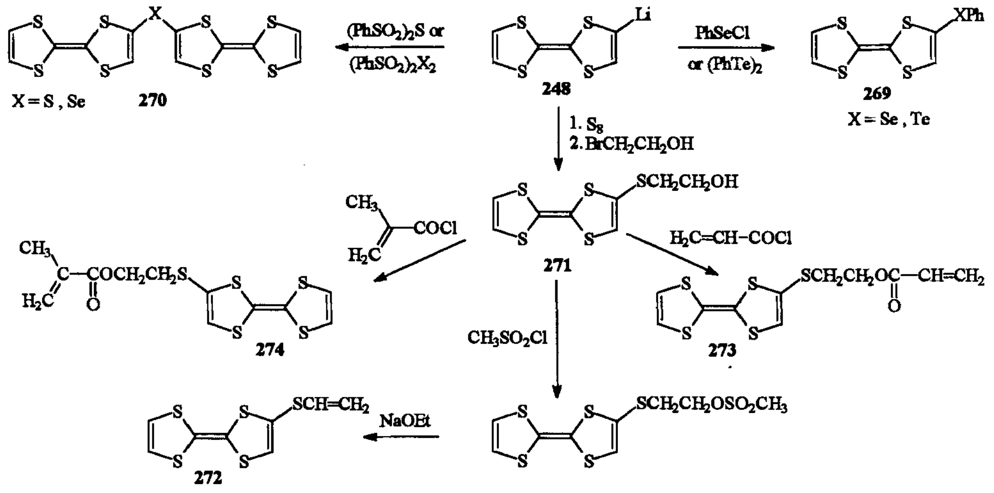
4,5-Dimethyltetrathiafulvalene cannot be halogenated using LDA as the lithiating agent and temperatures lower than −40°C. If a slight excess of butyllithium instead of LDA is used, the dihalogenated products can be prepared at −40°C or even lower by reaction with hexachloroethane, 1,2-dibromotetrafluoroethane or perfluorohexyl iodide [670].

Tetrathiafulvalenyllithium **248** forms with benzeneselenenyl chloride, phenylselenotetrathiafulvalene **269** (X = Se), and with diphenylditelluride, phenyltellurotetrathiafulvalene **269** (X = Te) [630,671].

Reaction of the monoanion **248** with bis(phenylsulfonyl) sulfide, bis(phenylsulfonyl) disulfide or bis(phenylsulfonyl) diselenide produces the corresponding sulfur or selenium bridged dimer bis(tetrathiafulvalenyl)sulfide **270** (X = S) or bis(tetrathiafulvalenyl)selenide **270** (X = Se) in moderate yield [672].

Lithiated trimethyltetrathiafulvalene affords with diethyl chlorophosphate the corresponding phosphonic diethylester, which can be converted to the bis(trimethylsilyl)ester by reaction with bromotrimethylsilane/triethylamine and then hydrolysed to the phosphonic acid [673].

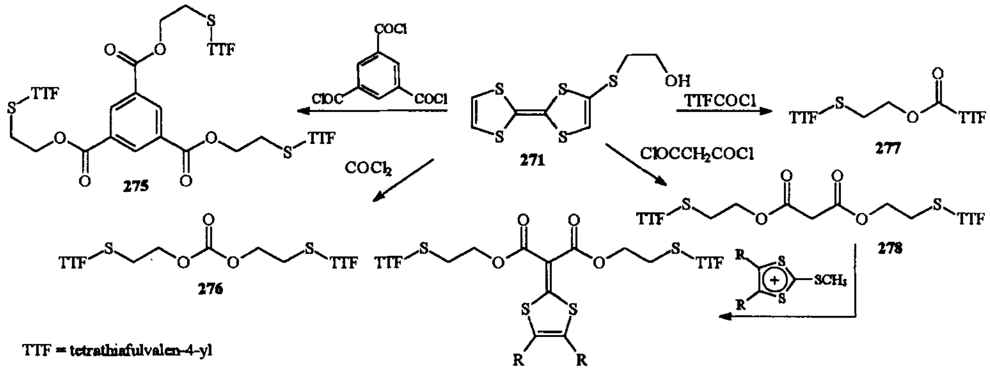
Reaction of monolithiotetrathiafulvalene **248** with elemental sulfur provides the thiolate anion (see [52] for a survey for preparation of thiolates), which can be alkylated with bromoethanol to the hydroxyethylthiotetrathiafulvalene **271**. Subsequent mesylation and treatment with sodium ethoxide gives vinylthiotetrathiafulvalene **272** [674]. Hydroxyethylthiotetrathiafulvalene **271** can be converted with acryloyl or methacryloyl chloride under basic conditions to the acrylate **273** or the methacrylate **274**, respectively.



SCHEME 153

Hydroxypropylthiotetrathiafulvalene derivatives react in the presence of DCC and 4-(dimethylamino)pyridine with a [60]fullerene acid and form TTF derivatives which are covalently linked to one, two or four C_{60} molecules [675].

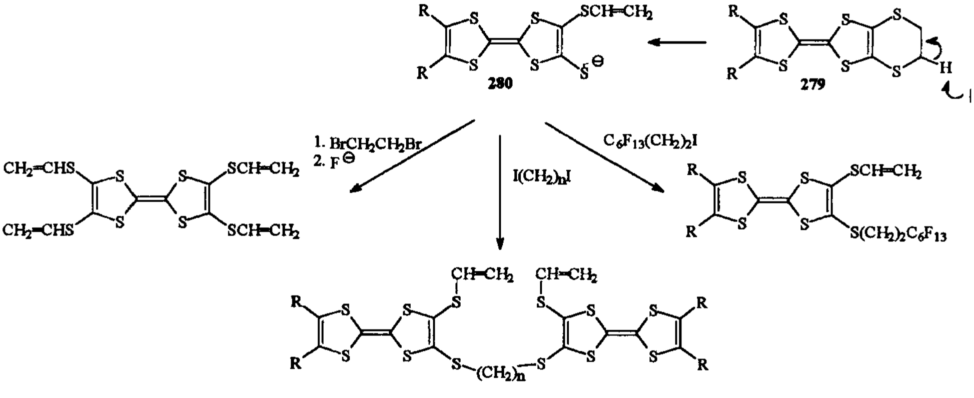
Hydroxyethylthiotetrathiafulvalene **271** can be used as an intermediate for further reactions. Conversion of the alcohol **271** with acid chlorides leads to bis- and tris (tetrathiafulvalenes) **275–278**, joined by ester linkages [676]. The hydroxyalkylthio substituent in TTF can be modified by reaction of the hydroxyethylthiotetrathiafulvalene **271** with alkyl- or acyl halides under basic conditions or by conversion of the methanesulfonyloxyethylthiotetrathiafulvalene with nucleophiles [210,677,678].



SCHEME 154

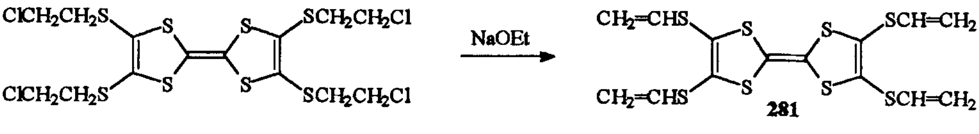
The vinylthio group is also formed by ring cleavage of the dithiacyclohexane ring under basic conditions. If ethylenedithio-tetrathiafulvalene **279** (R = H) is lithiated with two equivalents of LDA [679] or bis(ethylenedithio)tetrathiafulvalene **279**

[R = S(CH$_2$)$_2$] is treated with concentrated tetrabutylammonium fluoride [224, 227], the thiolate anion **280** is formed, which can be converted into new TTF-derivatives. In the case of the ring opening of ethylenedithio-tetrathiafulvalene with LDA the intermediate **280** could be isolated by reaction of the dilithiated species with *t*-butanol [680].



SCHEME 155

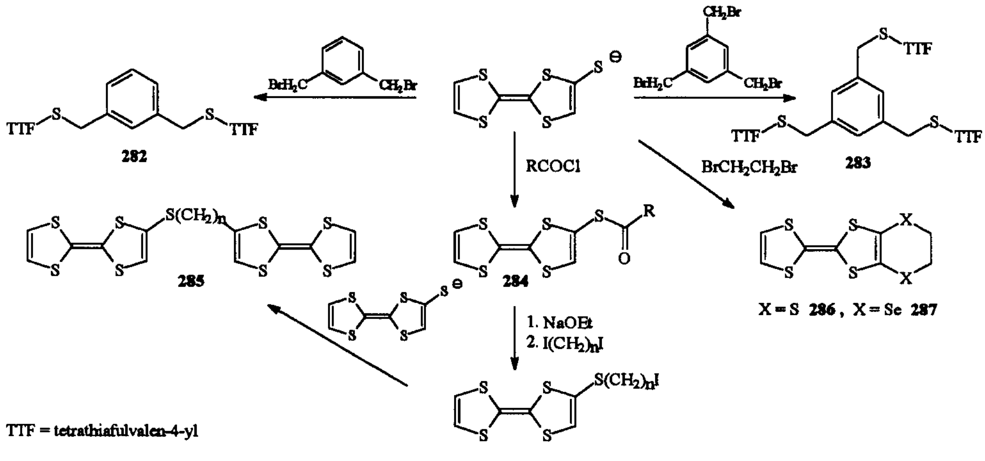
Base-induced elimination of hydrogen chloride from tetrakis(chloroethylthio)tetrathiafulvalene affords tetra(vinylthio)-tetrathiafulvalene **281**.



SCHEME 156

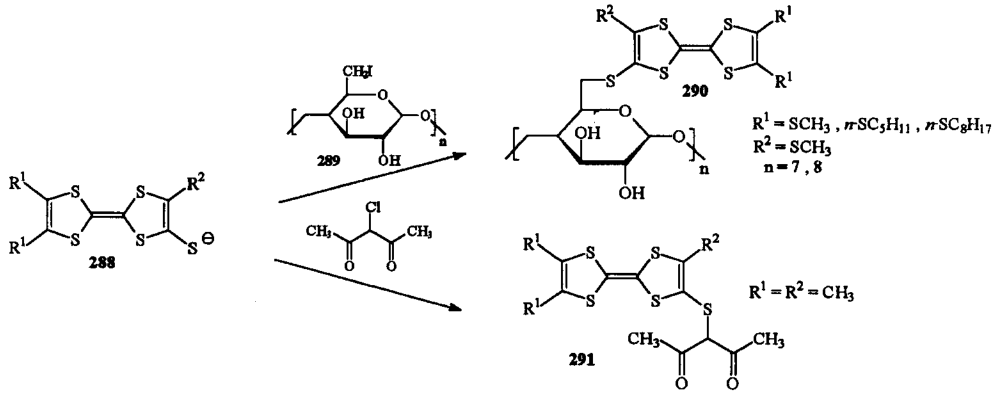
The TTF-thiolate anion can also be trapped with bis- and tris-halides to yield the bis- and tris(tetrathiafulvalenes) **282** and **283** [676]. The reaction of *in situ* generated substituted TTF-thiolate anion and an excess of 1,6-dibromohexane provides the corresponding bromoalkylthio-substituted TTF, which is further converted with 4-cyano-4′-hydroxybiphenyl into a 4′-cyanobiphenyl-4-yloxy-substituted TTF. Analogously a TTF derivative with four (4′-cyanobiphenyl-4-yloxy)hexylthio side groups was prepared which shows mesomorphic properties [681].

With acid halides the TTF-thiolate forms thioesters **284**, from which the thiolate anion can be regenerated with sodium ethoxide in ethanol at − 10°C. Reaction of the regenerated TTF-thiolate with diiodoalkanes provides bis-TTF **285** [676]. Surprisingly, the reaction of the TTF-monoanion with elemental sulfur or selenium (1.5 equiv.) and subsequent addition of 1,2-dibromoethane (0.5 equiv.) yielded ethylenedithiotetrathiafulvalene **286** and ethylenediselenotetrathiafulvalene **287** in yields of 10–20% [677].



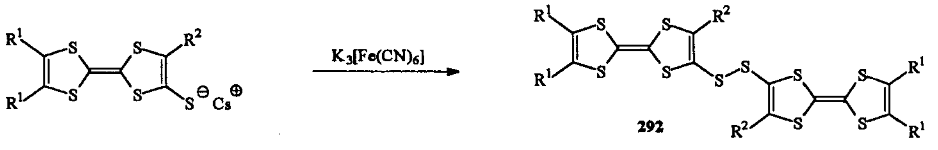
SCHEME 157

Substituted TTF-thiolate intermediates **288** react with periodo cyclodextrines **289** and form cyclodextrines **290** persubstituted with pendant tetrathiafulvalene moieties. These molecular assemblies allow an efficient access to Langmuir–Blodgett films, independently of their hydrophobic character [682,683]. With chloroacetylacetone TTF-thiolates **288** provides new TTF derivatives **291**. The acetylacetone unit opens broad application possibilities with the ketoenolate anion as chelating species [684].



SCHEME 158

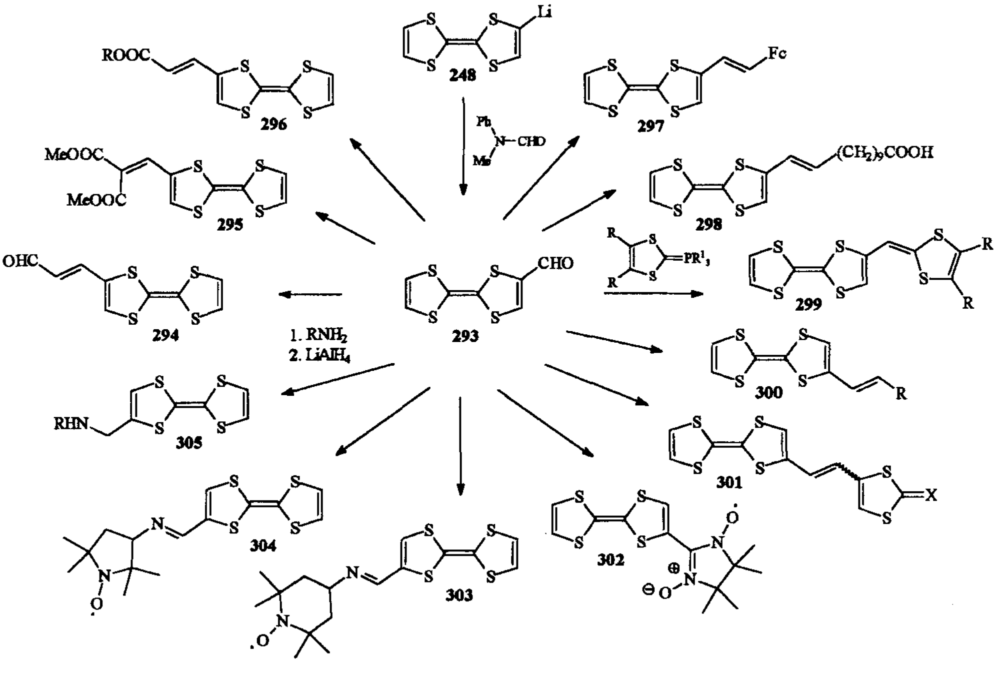
Oxidation of TTF-thiolate anions with aqueous potassium hexacyanoferrate(III) leads to the formation of tetrathiafulvalenyl disulfides **292** [685].



SCHEME 159

After development of an improved synthesis of formyltetrathiafulvalene **293**, this reactive TTF has been used as the key intermediate for the synthesis of new TTF derivatives. In the reaction of monolithiotetrathiafulvalene **248** with formylating agents (*N*,*N*-dimethylformamide, *N*-formylpiperidine, *N*-formylmorpholine, *N*-methylformamide, *N*-methyl-*N*-phenyl-formamide) with *N*-methylformamide [451] or *N*-methyl-*N*-phenylformamide [615] the highest yields (80%) of formyltetrathiafulvalene are obtained. Metallation of TTF with four equiv. of LDA and subsequent addition of 2.5 equiv. *N*-ethyl-*N*-phenylformamide yields tetrathiafulvalene-4,4′(5′)-dialdehyde [206].

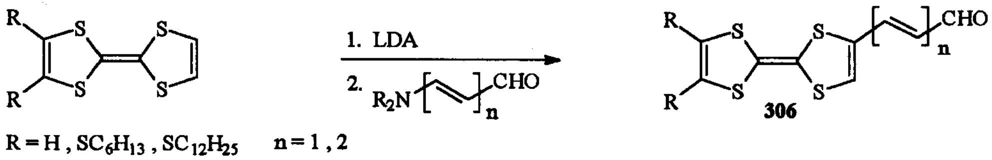
Formyltetrathiafulvalene **293** can be converted, by Wittig reactions or condensation reactions, to the new functionalized TTF-derivatives **294–296** [570,686], **297** [678], **298** [687], **299** [119,688], **300** [541,687,689,690], **301** [691], **302** [692], **303** [693], **304** [694], and **305** [695]. The TTF derivatives **302–304** contain a radical substituent and in CT-complexes of these compounds an interaction of the spins of the radical substituent with the spins in the donor and acceptor stacks is expected, resulting in materials with ferromagnetic properties [692–694,696,697]. In the same way bis- and tetrakis-radical substituted TTF derivatives with weak ferromagnetic interactions are synthesized [698].



SCHEME 160

Oxidation of the radical **302** provides the cation diradical with a singlet ground-state multiplicity due to distortion between the TTF radical cation unit and the nitronyl nitroxide radical unit. This unfavourable steric hindrance is released by inserting a 1,4-phenylene or 1,4-thiophenylene group between the TTF unit and the nitronyl nitroxide radical unit. One-electron oxidation of these radicals with iodine affords cation diradicals with a triplet ground state [647].

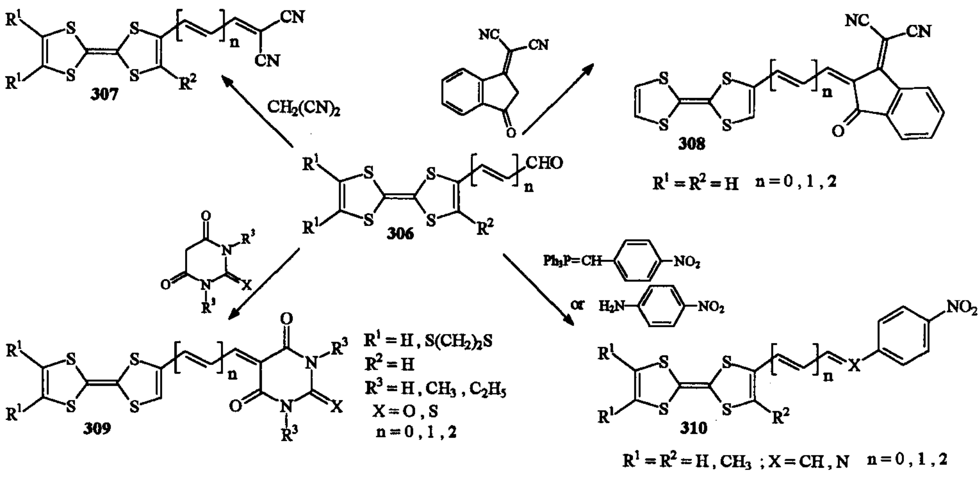
The formyltetrathiafulvalene vinylogue **294** or derivatives **306** are also synthesized by metalation of the TTF derivative with LDA and subsequent reaction with a vinylogous amide in a one-pot process [699].



SCHEME 161

In Knoevenagel reactions the formyltetrathiafulvalene vinylogues **306** form with strong C–H acid methylene components donor acceptor compounds, which show non-linear optical (NLO) properties. With malononitrile [699–701], 3-(dicyanomethylene) indan-1-one [702] or barbituric acid derivatives [703] the compounds **307**, **308** or **309** are formed, respectively. Analogously, 2-formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene vinylogues provide with malononitrile materials with NLO properties [704].

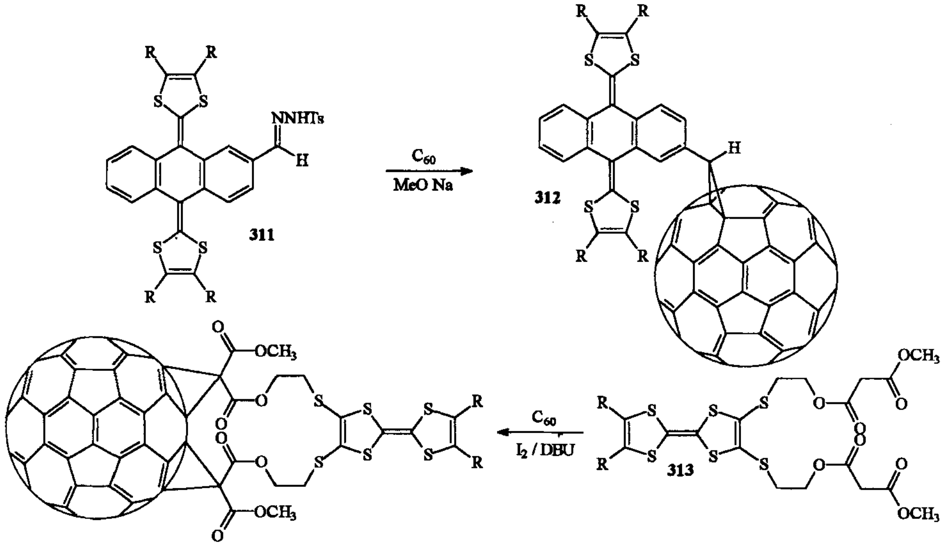
Wittig reagents yield with TTF derivatives **306** conjugated tetrathiafulvalene vinylogues **310** also with NLO properties [705].



SCHEME 162

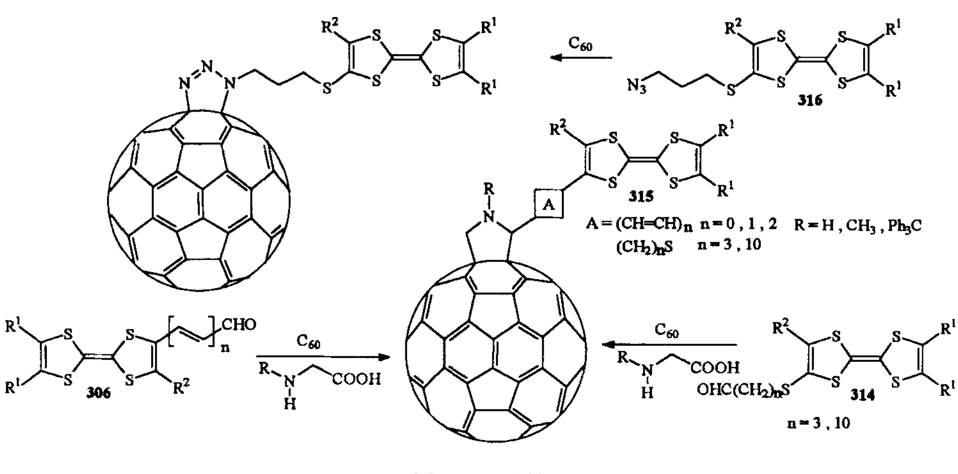
A covalent linking between 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives and C_{60} via cyclopropane is attained by cycloaddition of diazo compounds, generated *in situ* by treatment of the extended TTF containing 4-tosylhydrazones **311** with base, with C_{60}. In toluene at 70°C a mixture is formed of the two possible isomers of the [5,6]fulleroid, which can be converted by refluxing into the [6,6]methanofullerene **312**. The latter can be synthesized directly by refluxing of the 4-tosylhydrazones under basic conditions with C_{60} [706].

In a Bingel reaction of C_{60} with the TTF derivative **313** ($R = SC_{16}H_{33}$) in toluene in the presence of iodine and diazabicyclo-[5,4,0]undec-7-ene (DBU) the TTF core is directly attached to the C_{60} framework via two cyclopropane rings [707].



SCHEME 163

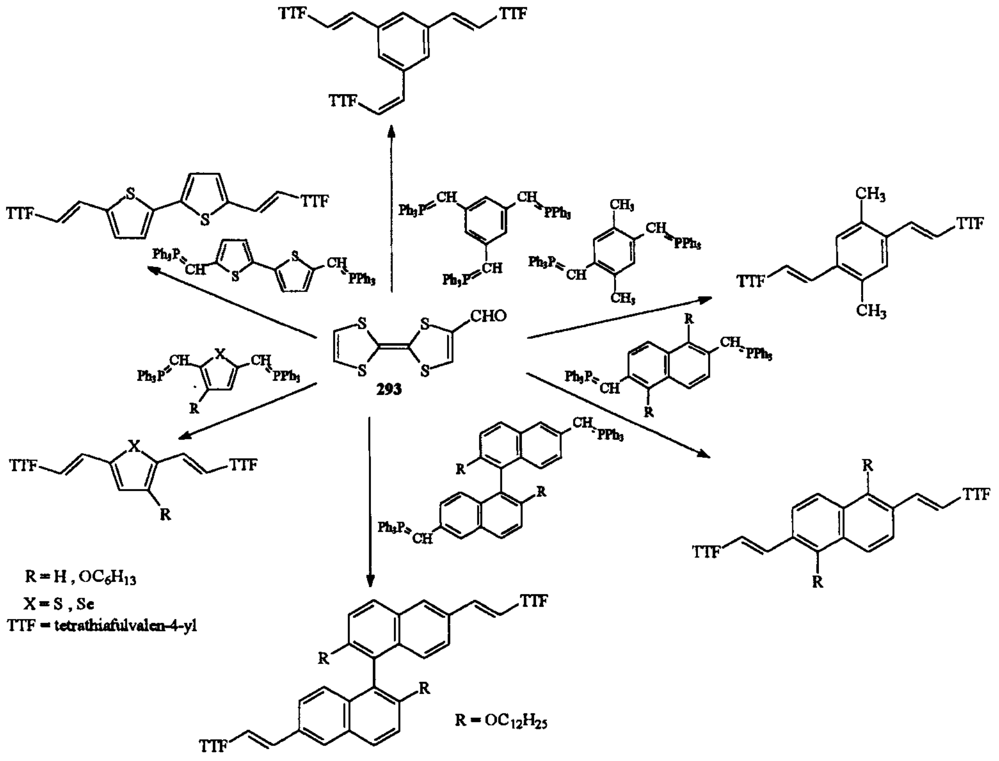
TTF can also be covalently linked via a pyrrolidine heterocyclus with [60]fullerene by treating formyltetrathiafulvalene **293** or substituted derivatives **306**, or **314**, an amine and [60]fullerene in refluxing toluene. In a 1,3-dipolar cycloaddition of azomethine ylides forms the connection at the 6,6-ring junction of the C_{60} framework to form **315** [708–712]. In the same manner highly conjugated TTF derivatives with 1,4-quinodimethane structure are covalently attached to C_{60} [713–715]. The reaction of a TTF azide **316** with C_{60} in 1,2-dichlorobenzene at 60°C leads to a covalent linking between the TTF moiety and C_{60} via a triazoline heterocyclic intermediate [716].



SCHEME 164

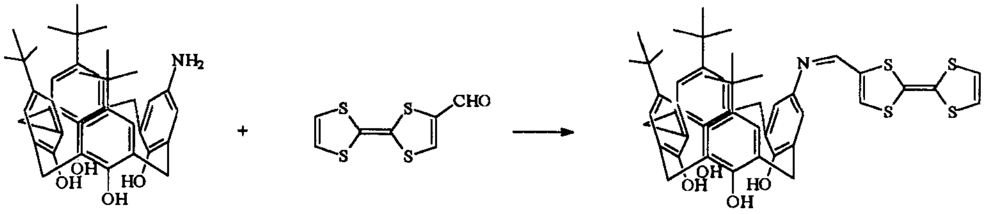
In these dyads between C_{60} and covalently attached TTF derivatives via different bridges the fullerene singlet excited state is quenched by electron transfer and forming of the charge-separated radical pair $C_{60}^{\bullet -}$-$TTF^{\bullet +}$ [706,707,712,714–716].

In Wittig reactions with di- or trivalent phosphoranes formyltetrathiafulvalene **293** provides TTF with conjugated spacers between TTF-moieties [451,689,717–723].



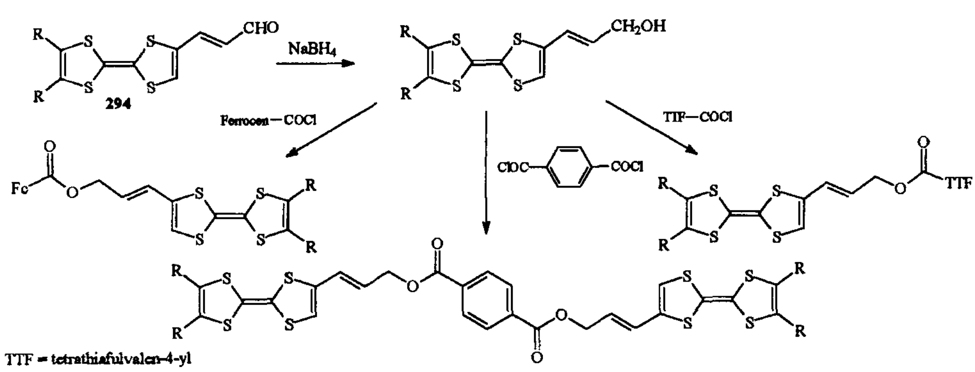
SCHEME 165

Via formation of an azomethine the TTF moiety is connected with a tri-*t*-butyl-calix[4]arene (53% yield) [724].



SCHEME 166

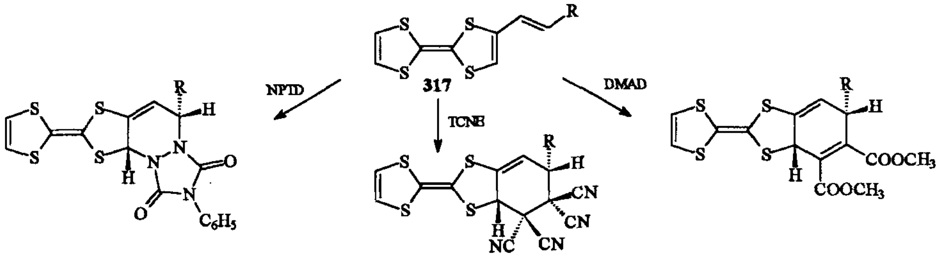
The conjugated TTF-aldehydes **294** can also be reduced with sodium borohydride to the corresponding alcohols, which are further converted by acid chlorides into esters [570,725].



TTF = tetrathiafulvalen-4-yl

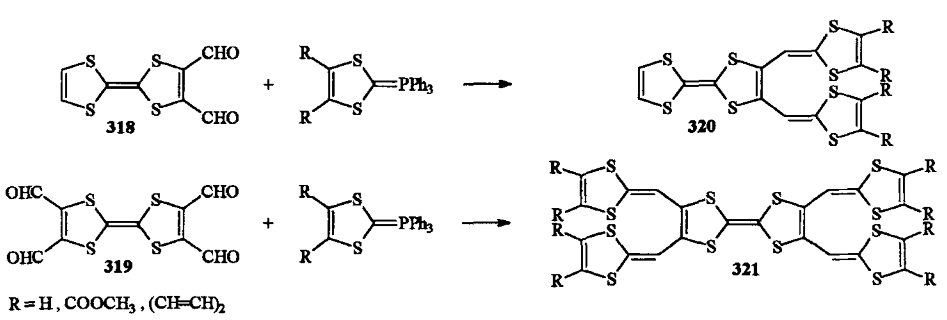
SCHEME 167

By appropriate Wittig reactions vinyl-TTF derivatives **317** (purified *trans* isomer) act as dienes in Diels–Alder reactions. With acceptors like tetracyanoethylene (TCNE), *N*-phenyl-1,2,4-triazoline-3,5-dione (NPTD) or dimethyl acetylenedicarboxylate (DMAD) they do not form charge-transfer complexes, but give [4 + 2]cycloaddition 1 : 1 adducts [726].



SCHEME 168

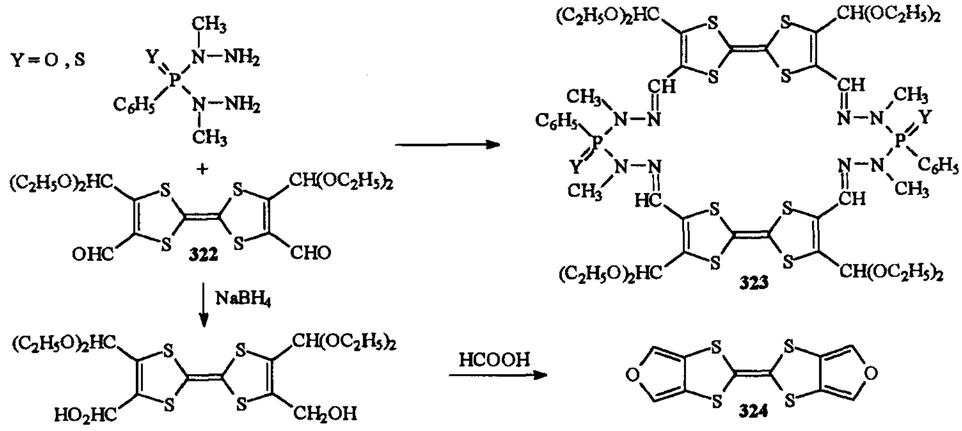
In an analogous manner to **293** multi-formyl-TTF form olefinic bonds upon treatment with phosphoranes. Wittig reactions of 4,5-diformyltetrathiafulvalene **318** and tetraformyltetrathiafulvalene **319** with phosphoranes produces bis- and tetrakis-(1,4-dithiafulvenyl)tetrathiafulvalenes **320** and **321** in yields of 70–80% [727].



R = H, COOCH3, (CH=CH)2

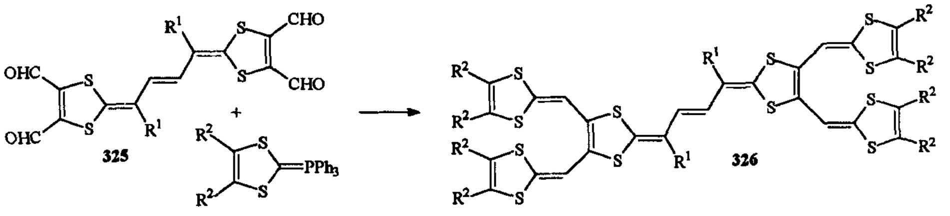
SCHEME 169

Treatment of the *cis*-isomer of the diacetalized tetraformyltetrathiafulvalene **322** with phosphodihydrazides (Y = O, S) leads to macrocycles **323** in yields of 80% and 60%, respectively [728]. The aldehyde groups in the TTF **322** are reduced with $NaBH_4$ to the corresponding alcohol and subsequent formolysis provides the fused furano TTF **324** [729].



SCHEME 170

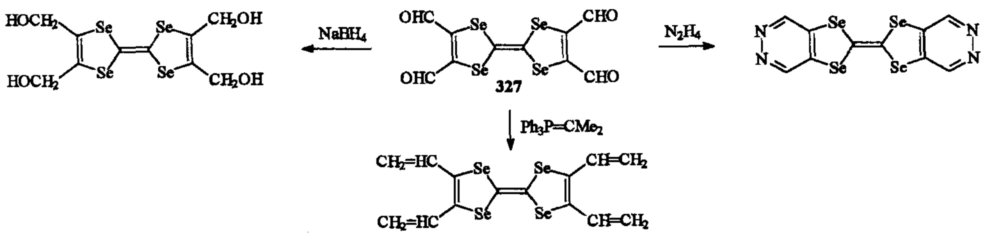
Also tetraformyl substituted vinylogues of TTF **325** react with phosphoranes or phosphonate anions to give TTF derivatives **326** with a more extended π-system [730].



$R^1 = H, C_6H_5, C_6H_4CH_3\text{-}4 \quad R^2 = H, COOCH_3, (CH{=}CH)_2$

SCHEME 171

Tetraformyltetraselenafulvalene **327** is an efficient precursor for heteroannelated and tetrasubstituted TSF [397].



SCHEME 172

Multilithiated TTF are formed when the lithiation is carried out at −20°C or when excess of lithiation reagent is used [629]. The treatment of multilithiated TTF with reagents provides multisubstituted TTF.

Tetralithiated TTF **328** [731] has been chlorinated and brominated with hexachloroethane and 1,2-dibromotetrachloroethane, respectively (yield 15%) [670,732]. Tetrabromo-TTF is prepared in a simpler way and in high yield (97%) by bromination of tetrathiafulvalene with a mixture of bromine/48% hydrobromic acid in ether [733]. When perfluorohexyl iodide was used as the halogenating agent no tri- or tetraiodo-TTF derivatives could be obtained [634]. Lithiation of the TTF with ten equivalents of LDA and iodination with iodine provides the tetraiodo derivative (yield 26%) along with the diiodotetrathiafulvalene (yield 11%) [655]. After tetralithiation with phenyllithium, and using iodine as the halogenating agent, none of the desired product was obtained [732].

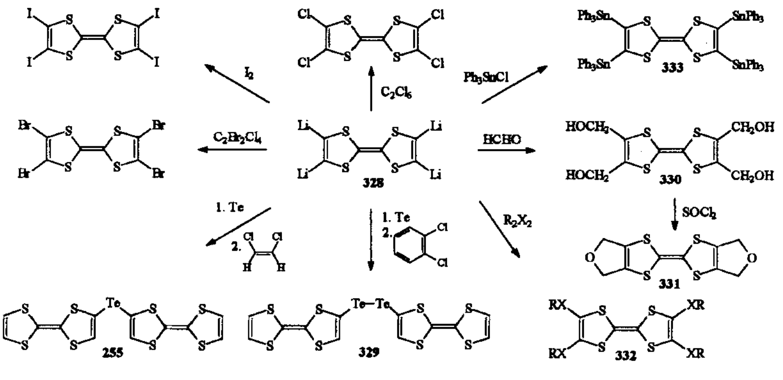
After treatment of tetralithiated TTF **328** with tellurium and subsequent reaction with *cis*-dichloroethene the bis(tetrathiafulvalenyl)telluride **255** is formed in 20% yield, and not the unsaturated telluro analogue of bis(ethylenedithio)-TTF [642]. With 1,2-dichlorobenzene the TTF tetratellurolate anion yielded the unexpected ditelluride **329** instead of the anticipated fused system [734].

The intermediate tetralithiotetrathiafulvalene **328** reacts with formaldehyde and provides tetrakis(hydroxymethyl)tetrathiafulvalene **330**, which can be converted with thionyl chloride into bis(oxydimethylene)tetrathiafulvalene **331** [735].

The tetrakis(alkylchalcogeno)tetrathiafulvalenes or tetrakis(arylchalcogeno)tetrathiafulvalenes **332** (X = S, Se, Te) can be prepared in good to excellent yield (64–90%) by reaction of tetralithiotetrathiafulvalene **328** with various dialkyl or diaryl disulfides, diselenides, or ditellurides as electrophiles [630,736,737]. When the lithiation and the subsequent reaction are performed with four equivalents of LDA and benzeneselenenyl chloride the corresponding di-, tri-, and tetrasubstituted TTF can be isolated after chromatographic separation [671],

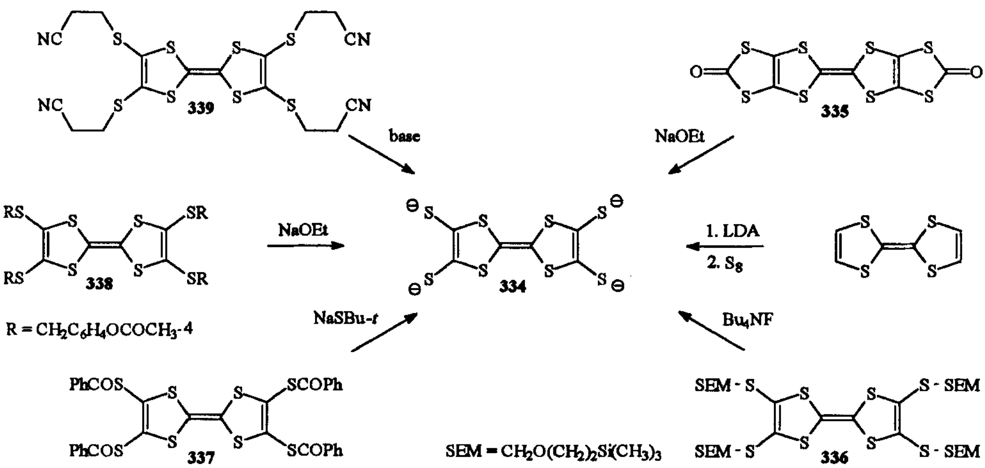
Lithiation of TTF with ten equivalents of LDA and following reaction with chlorotriphenyltin gives tetrakis(triphenylstannyl)-tetrathiafulvalene **333** (yield 30%) [655].

TTF-tetrathiolate **334** is a key intermediate in the synthesis of thio-substituted TTF. This intermediate has been prepared in different ways [52]. Firstly the dithiapendione **335** is hydrolysed with sodium ethoxide in refluxing ethanol or methyllithium in tetrahydrofuran at room temperature [601]. Later TTF-tetrathiolate **334** is formed by treatment of TTF with 4 equiv. of LDA, followed by 4 equiv. of sulfur [731]. This method was improved by use of excess base (10 equiv. LDA). In that way a higher yield and a purer product could be obtained [629].



SCHEME 173

Furthermore, some precursors with protecting groups can be deprotected by treatment with nucleophiles affording the TTF-tetrathiolate **334**. Tetrakis(trimethylsilylethoxymethylthio)tetrathiafulvalene **336** is converted into TTF-tetrathiolate **334** by reaction with tetrabutylammonium fluoride in tetrahydrofuran at room temperature [224]. Sodium *t*-butylthiolate in tetrahydrofuran reacts at − 10°C with tetrakis(benzoylthio)tetrathiafulvalene **337** and provides TTF-tetrathiolate **334** [129,738]. The 4-acetoxybenzylthio protecting group in the corresponding TTF **338** can be removed with sodium ethoxide in ethanol [335,336]. Strong bases such as sodium ethoxide in ethanol or sodium hydride in DMF or tetrabutylammonium hydroxide, methyllithium, LDA, potassium *t*-butoxide or cesium hydroxide remove the cyanoethyl group in the TTF **339** [332]. The advantage of the latter procedure is the synthesis of the precursor **339** on a large scale (> 20 g) in high yield from inexpensive starting materials. Especially the facile stepwise cleavage of the cyanoethyl group by treating with different equivalents of cesium hydroxide monohydrate in methanol and subsequent quenching of the thiolate with a variety of electrophiles leads to a broad application of this method. Many new macrocyclic and supramolecular systems incorporating the TTF moiety are prepared [52].



SCHEME 174

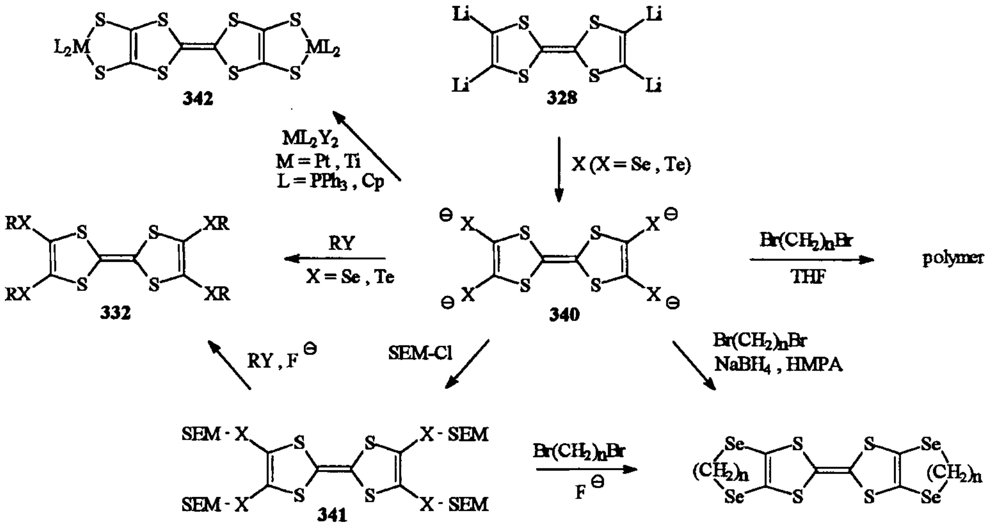
TTF-tetrathiolate **334** can react with alkyl halides or inorganic salts to form alkylthio substituted TTF or coordination complexes of TTF.

TTF-tetraselenolate or TTF-tetratellurolate is prepared by tetralithiation of TTF and subsequent insertion of selenium or tellurium into the carbon lithium bonds of tetralithiotetrathiafulvalene. Attempts at intramolecular alkylative ring closure of the selenium and tellurium derivatives **340** (X = Se, Te) with dibromoalkanes only lead to polymeric products. Obviously, these are formed by predominantly intermolecular alkylation, even at high dilution or at low temperatures [739]. In order to solve this problem, the TTF-tetrachalcogenolate anions **340** have been converted into stable intermediates by introduction of protective groups, a convenient blocking reagent being 2-(trimethylsilyl)ethoxymethyl chloride (SEM-Cl). Removal of the SEM groups proceeds with tetrabutylammonium fluoride at a lower rate compared to the alkylation of selenolate anions with dibromoalkanes, thus promoting cyclization over polymerization. With 1,2-dibromoethane or dibromomethane as alkylating agent alkylselenotetrathiafulvalene are obtained in good yields (30–35%). Similar results are obtained by introducing the cyanoethyl group as protective group. Removal of the four cyanoethyl groups with potassium *t*-butoxide in DMF and alkylation with 1,3-dibromopropane or 1,3-dibromo-2-methylpropane provides the corresponding TTF in moderate yields (19 and 25%, respectively) [659].

In the case of the TTF-tetratellurolate anion tetrakis(SEM-telluro)tetrathiafulvalene **341** (X = Te) is produced in good yield (63%), but reaction with dibromoalkanes in the presence of tetrabutylammonium fluoride fails to provide the desired products [739]. The formation of polymers in the reaction of TTF-tetraselenolate anions **340** (X = Se) with dibromoalkanes is attributed to the poor solvation of the TTF-tetraselenolate anions in the solvent used so far (THF). It has been speculated that, if the TTF-tetraselenolate anion is sufficiently solvated, the dibromoalkane molecule enters the solvent sphere of the solvated TTF-tetraselenolate anion and reacts with the anion within the solvent sphere faster than with one outside the solvent sphere. In fact replacement of THF by hexamethylphosphoramide (HMPA), a dipolar aprotic solvent, allows the bis(alkylseleno)tetrathiafulvalene to be formed in good yields (25–65% after recrystallization). Addition of sodium borohydride eliminates the formation of some polymeric by-products by cleavage of Se–Se linkages formed by oxidation of the TTF-tetraselenolate anions [740].

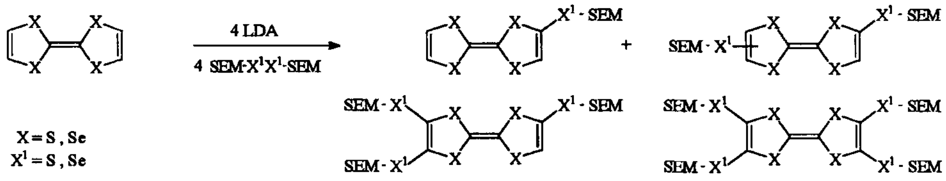
Reaction of the TTF-tetrachalcogenolate anions **340** as well as a reaction of tetrakis(SEM-chalcogeno)tetrathiafulvalene **341** after removal of the protecting group by tetrabutylammonium fluoride with alkyl halides yields the tetrakis(alkylchalcogeno)-tetrathiafulvalene **332** [632,741–744].

Transition metal homobimetallic coordination complexes **342** of TTF-tetrathiolate are formed by reaction of TTF-tetrathiolate **340** (X = S) with titanocene dichloride, substituted titanocene dichlorides, bis(triphenylphosphine)platinum(II) chloride or nickel salts [392,745,746].



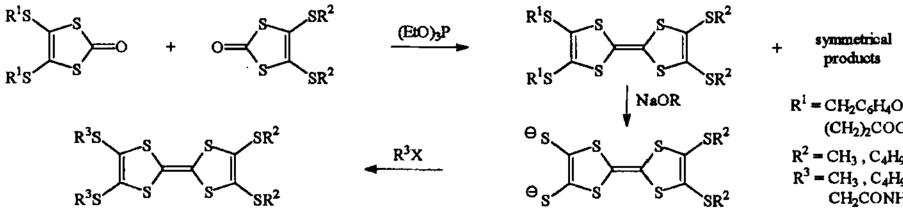
SCHEME 175

The removal of the protecting SEM-group with tetrabutylammonium fluoride opened up the possibility of the synthesis of asymmetrically substituted tetrachalcogenafulvalenes. The lithiated TXF is treated with SEM disulfide or SEM diselenide and affords all four types of the X^1-SEM substituted TXF in an overall yield of 66–75% [747]. This product mixture can be easily separated on a silica gel column. Reaction of the separated products with anhydrous tetrabutylammonium fluoride in THF in the presence of alkyl bromides provides the desired compounds in a very pure form.



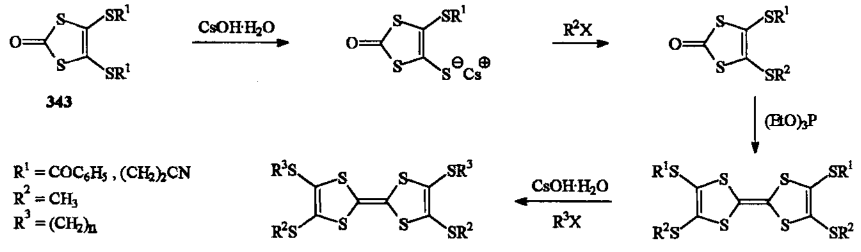
SCHEME 176

Asymmetrical TTF have also been synthesized with 4-acetoxybenzyl [335,336] or ethoxycarbonylethyl [748] as a blocking group. After cross-coupling of two 1,3-dithiol-2-ones the resulting product mixture is separated by column chromatography. The protecting group is then removed with sodium ethoxide in ethanol or sodium *t*-butylthiolate in tetrahydrofuran at −10°C [335,336] or with sodium methoxide in methanol/dichloromethane (9 : 1) at room temperature via a retro-Michael addition [748]. The dithiolate thus formed is then quenched with alkyl halides.



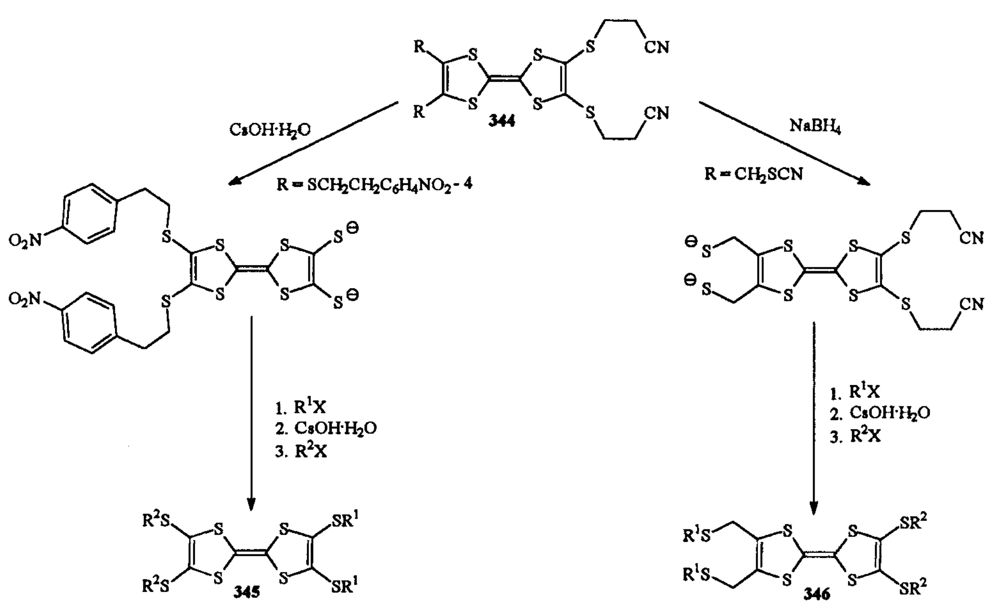
SCHEME 177

Treatment of protected 1,3-dithiole-2-thione-4,5-dithiolates **343** with one equivalent of cesium hydroxide gives selectively and in high yields the corresponding monocesium salts. The cesium salts are more air and moisture stable than the other alkali metal salts and can subsequently be alkylated. Following dimerization with triethyl phosphite yields the unsymmetrically substituted TTF, which can be further converted by deprotecting/alkylation reactions [333,349,362,370,749,750].



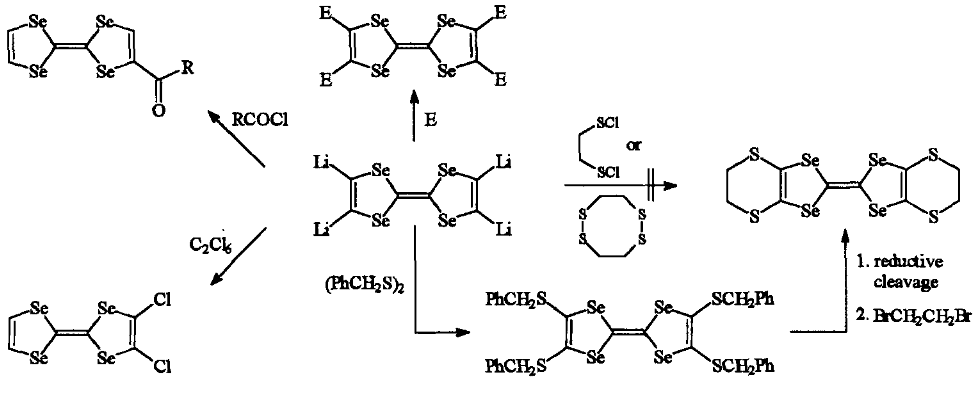
SCHEME 178

Cross-coupling of two 1,3-dithiol-2-ones or -thiones with triethyl phosphite, bearing two different protecting groups, give asymmetric TTF derivatives **344**. Selective deprotection open the possibility to functionalize the TTF moiety regioselectively in the 4- and 5-position, followed by a functionalization of the TTF moiety in the 4′- and 5′-position. So firstly in the TTF **344** ($R = SCH_2CH_2C_6H_4NO_2$-4) the cyanoethyl group is deprotected with cesium hydroxide. After alkylation, deprotection of the 4-nitrophenylethyl group with further cesium hydroxide and alkylation asymmetric substituted TTF derivatives **345** are formed [751]. Asymmetric substituted TTF derivatives **346** are synthesized by reduction of **344** ($R = CH_2SCN$) with sodium borohydride, alkylation, deprotection of the cyanoethyl group with cesium hydroxide and alkylation [212].



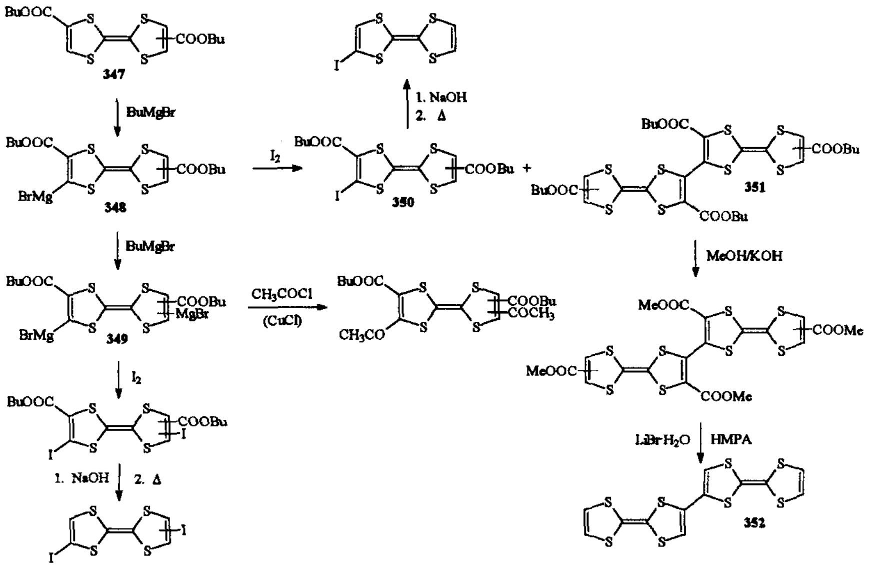
SCHEME 179

TSF can also be converted with LDA into the tetralithio derivative. Treatment of TSF with *n*-butyllithium under conditions employed with TTF led to total destruction of the TSF framework [752]. Reaction of tetralithiotetraselenafulvalene with excess of electrophile (Me_2S_2, Ph_2S_2, Me_2Se_2, Ph_2Se_2, ClCOOMe, CO_2) affords the corresponding tetrasubstituted TSF in moderate yields (30–70%) [743,752,753]. The reaction with 1,2-disulfenyl chlorides or 1,2,5,6-tetrathiocyclooctane does not provide bis(ethylenedithio)tetraselenafulvalene. The route via the tetrabenzylthio intermediate (yield over 50%) via subsequent reductive cleavage and alkylation with 1,2-dibromoethane is promising [754]. By addition of less than one equivalent acid chloride to tetralithiated TSF the monoacyltetraselenafulvalene derivative is the only isolated product (14–20% yield) besides regenerated TSF [755]. By lithiation with four equivalents of LDA and subsequent reaction with hexachloroethane only the 2,3-dichloro TSF is formed [421].



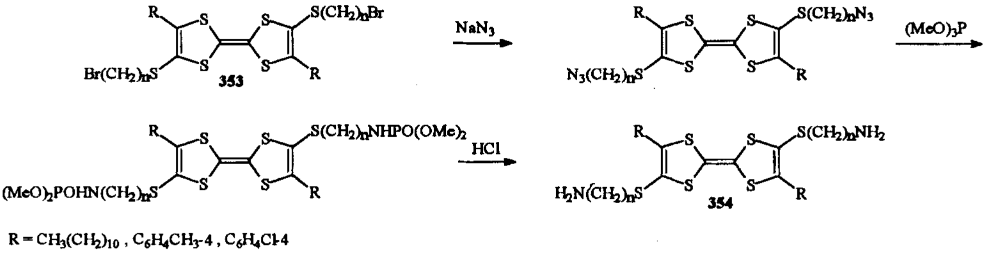
SCHEME 180

Metallation of TTF derivatives can also be achieved with Grignard agents [756]. Treatment of bis(butoxycarbonyl)tetrathiafulvalene **347** with butylmagnesium bromide gives the monometallated derivative **348**, and on further reaction with butylmagnesium bromide the dimetallated derivative **349**. Both react readily with electrophiles, e.g. acetyl chloride, 2-chloroethyl formate or iodine, and provide the corresponding derivatives. In the reaction of bis(butoxycarbonyl)-tetrathiafulvalenylmagnesium bromide **348** with iodine a mixture of two products is formed, a monoiodo substituted TTF **350** (37%) and a dimerized TTF derivative **351** (25%). The butoxycarbonyl group in the TTF derivatives can be hydrolysed in a refluxing alkaline mixture of water and dioxan. Upon heating in diglyme the acid decarboxylates. With methanol in alkaline solution the butoxycarbonyl group is converted into a methoxycarbonyl group. Demethoxycarbonylation with lithium bromide monohydrate at 150°C provides the unsubstituted dimerized TTF **352**.



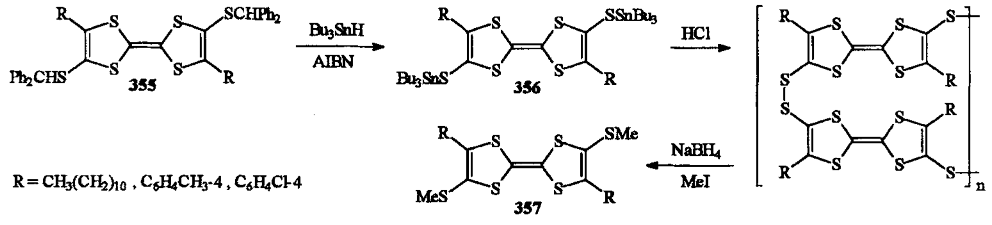
SCHEME 181

The synthetic route to TTF via mesoionic 1,3-dithioles made it possible to prepare many substituted TTF derivatives, which in turn can be converted into new derivatives [194]. Thus, the bis(aminoalkylthio)tetrathiafulvalene **354** ($n = 3, 6$) are obtained by nucleophilic substitution of the bis(bromoalkylthio)tetrathiafulvalene **353** with sodium azide in DMSO, followed by treatment with trimethyl phosphite and subsequent hydrolysis with hydrochloric acid.



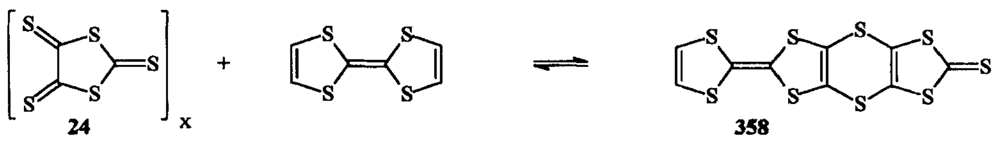
SCHEME 182

In a radical initiated reaction the bis(benzhydrylthio)tetrathiafulvalene **355** are treated with tributylstannane and provide bis(tributylstannylthio)tetrathiafulvalene **356**. Further reaction with gaseous hydrogen chloride leads to S–S bond formation and formation of polymeric TTF. The S–S linkages of polymeric TTF can be cleaved with sodium borohydride and alkylated with methyl iodide to form the di(methylthio) tetrathiafulvalene **357** [194].



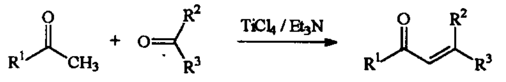
SCHEME 183

The oligomeric 1,3-dithiole-2,4,5-trithione **24**, which presumably depolymerizes on heating, can be added to TTF to form the cycloadduct **358** in 30–50% yield. The reaction is reversible and in boiling toluene 60–65% TTF can be recovered [757].



SCHEME 184

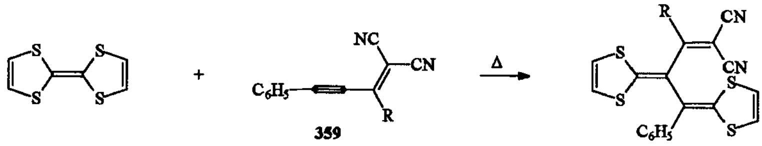
With $TiCl_4/Et_3N$ as the condensation reagent, chalcones with TTF as a substituent can be prepared [758].



$R^1 = TTF, C_5H_4FeC_5H_5, C_6H_5Cr(CO)_3$
$R^2 = TTF, C_5H_4FeC_5H_5, C_6H_5Cr(CO)_3, C_6H_5$
$R^3 = CH_3$

SCHEME 185

The dicyano(ethynyl)ethenes **359** and TTF do not form charge transfer complexes, but new covalent compounds [759]. Probably the reaction begins with a [2 + 2] cycloaddition of the triple bond to the central double bond of the TTF and formation of a cyclobutene derivative, which is stabilized by ring opening.

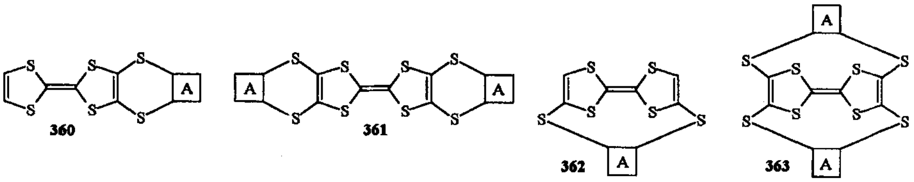


$R = H, COOC_2H_5, CN, C{\equiv}C{-}C_6H_5$

SCHEME 186

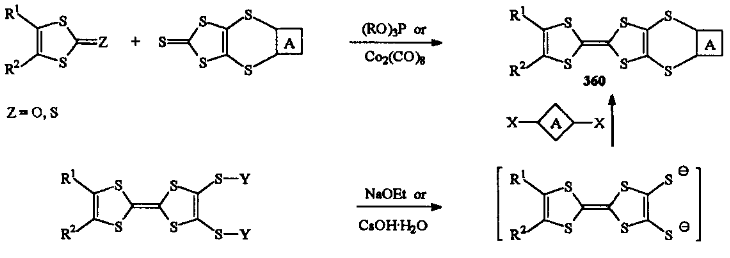
7.1.1. *Formation of Mono- and Bismacrocycles*

Tetrathiafulvalene can be substituted in four positions and therefore the TTF framework can be incorporated in mono- or bicyclic compounds **360–363**.



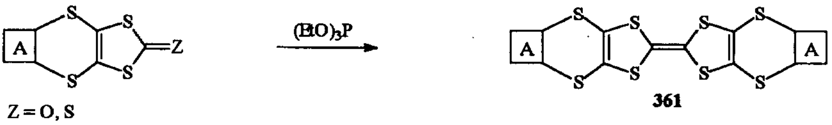
SCHEME 187

The compounds **360** are synthesized by cross-coupling of the corresponding 1,3-dithiol-2-ones or -thiones with trimethyl or triethyl phosphite [293,760] or dicobaltoctacarbonyl [293] and subsequent separation of symmetrical products by column chromatography. The yields are increased by reaction of protected tetrathiafulvalenedithiolates ($Y = CH_2CH_2CN$, $CH_2C_6H_4OCOCH_3$-4) with sodium ethoxide [336,761, 762] or cesium hydroxide [365], followed by realkylation with divalent nucleophiles. 4,5-Diaminoalkyl- or -dihydroxyalkyl-substituted TTF form with pyromellitic dianhydride TTF monomacrocycles **360** [356].



SCHEME 188

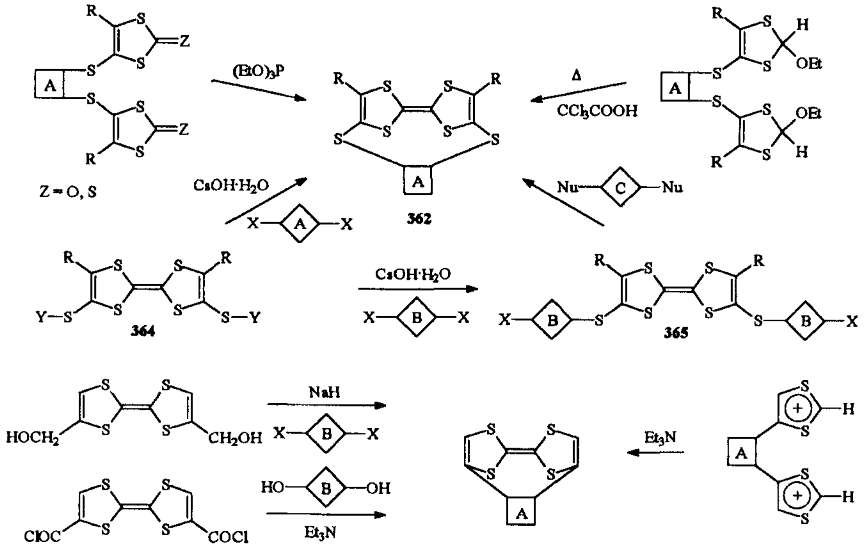
A series of oxygen, sulfur, and nitrogen TTF crowns or polymethylene TTF **361** ('bow tie' [763]) are formed by intermolecular phosphite coupling of the 1,3-dithiol-2-ones [764] or -thiones [253,760,765–773]. TTF crowns **361** form complexes with metal ions indicated by changes in the electronic absorption spectrum and anodic shift of the first oxidation potential [293,767,770,773–775]. Crown ether TTF, modified by bis(thioctic ester) derivatives, form stable self-assembled monolayers on gold electrodes and can recognize sodium- and potassium ions by cyclic voltammetry [774].



SCHEME 189

TTF derivatives **362** bridging the 4,4′(5′)-position of the TTF moiety are prepared by intramolecular coupling of bis(1,3-dithiol-2-ones) or -thiones [348,362,615,749], bis(2-ethoxy-1,3-dithioles) [347,353] or bis(2*H*-1,3-dithiolium) salts [776].

Bridged bis(1,3-dithiolyl)diphosphonate anions react with anthraquinone and form the corresponding bridged 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives [777]. Deprotection of TTF **364** (Y = CH_2CH_2CN) with cesium hydroxide and reaction of deprotected dithiolates with one equivalent of dihalide provides, under high-dilution conditions, directly TTF monomacrocycles **362** [348,354,355,359, 362,365,370,371,750,778,779], which can also be synthesized by deprotection of TTF **364** with cesium hydroxide, conversion with two equivalents of dihalide in a new bishalide **365** and subsequent reaction with one equivalent of a bisnucleophile [349,365,750, 780,781]. In a similar reaction the dianion of a pyrrolo-annelated TTF provides with one equivalent of dihalide under high-dilution conditions to give pyrrolo-annelated TTF monomacrocycles [782].

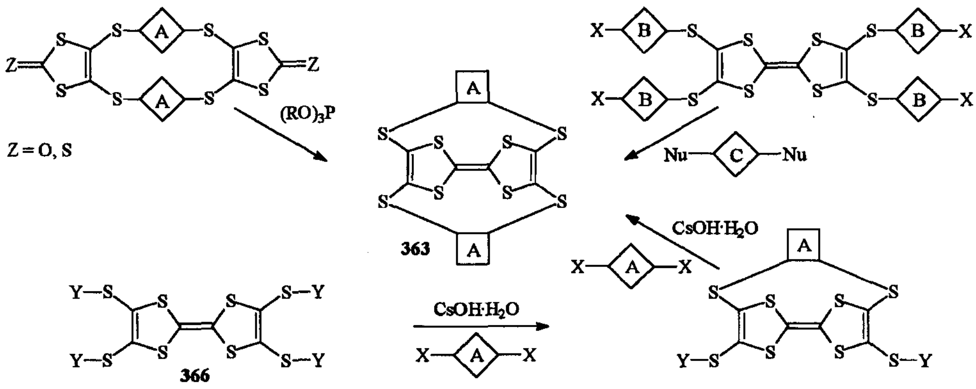


SCHEME 190

A dihydroxy TTF [783] and TTF diacid dichloride [784] yields with one equivalent of dihalide or dialcohol the corresponding TTF monomacrocycles, respectively. In the same way a 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivative with two hydroxymethyl groups in the 4,4′(5′)-position of the TTF unit forms with diacid dichlorides a series of monocycles [785]. As opposed to this bridging across the dithiole rings, a bridging across the 2,6-position of the anthracene unit is attained by reaction of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives with hydroxy functions in the 2,6-position of the anthracene moiety and 1,4-phenylenedicarbonyl dichloride [786]. Under Mitsunobu conditions (Ph_3P, ethyl azodicarboxylate) dihydroxy TTF reacts with pyromellitic dianhydrides to form TTF derivatives **362** [356].

Mostly a *cis/trans* mixture of **362** is formed, which could be separated only in a few cases (see Section 1.11).

TTF bismacrocycles **363** (‘cage’ [773]) are prepared by intramolecular coupling of 1,3-dithiol-2-ones or -thiones with trialkyl phosphites in solution [765,768,770,772, 773,787–790]. In a one-pot reaction **363** is also formed by treatment of tetrahalides with two equivalents of a bisnucleophile [791–793]. The protected TTF tetrathiolate **366** ($Y = CH_2CH_2CN$) is converted, in a two-step deprotection/cyclization reaction under high-dilution conditions, to TTF derivatives **363** [362,363,778,794]. The monomacrocycles, so formed in the first step, can be converted with a different bishalide into bismacrocycles with two different bridges [362].



SCHEME 191

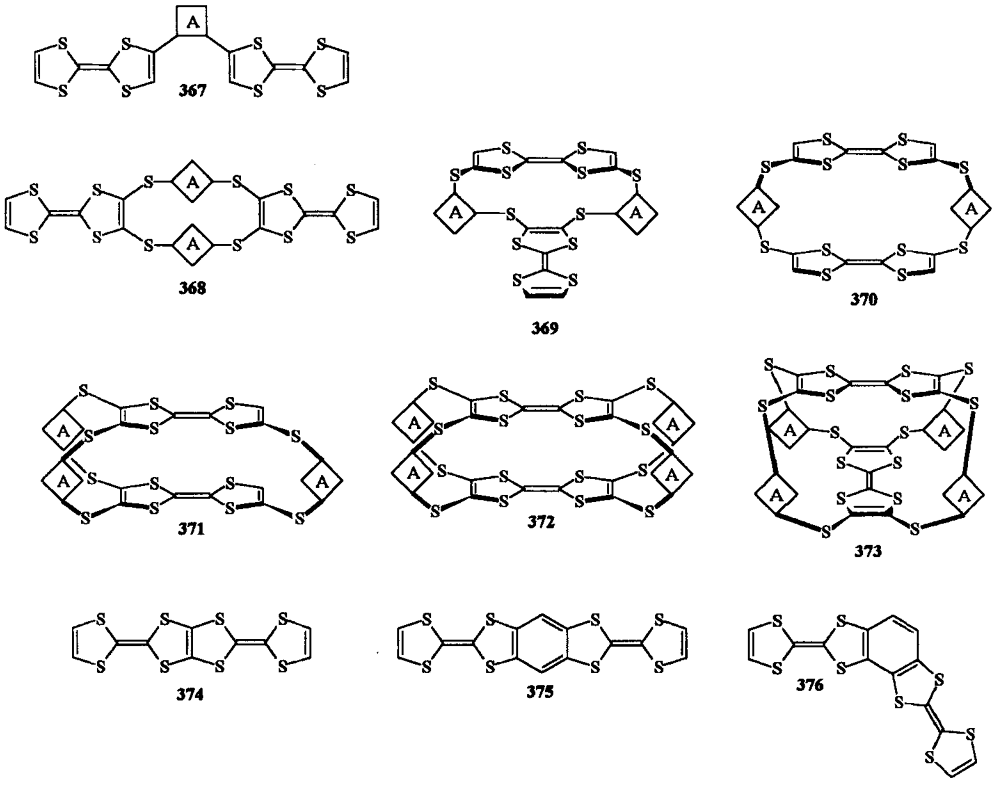
7.1.2. *Formation of TTF Dimers*

TTF dimers can be divided into four classes based on the number and position of the linkage of the spacer groups [51,55].

1. Single-linkage of type **367**
2. Double-linkage of type **368**, **369**, **370**
3. Triple-linkage of type **371**
4. Quadruple-linkage of type **372**, **373**

Moreover the condensed types of TTF dimers **374**, **375**, **376** are synthesized.

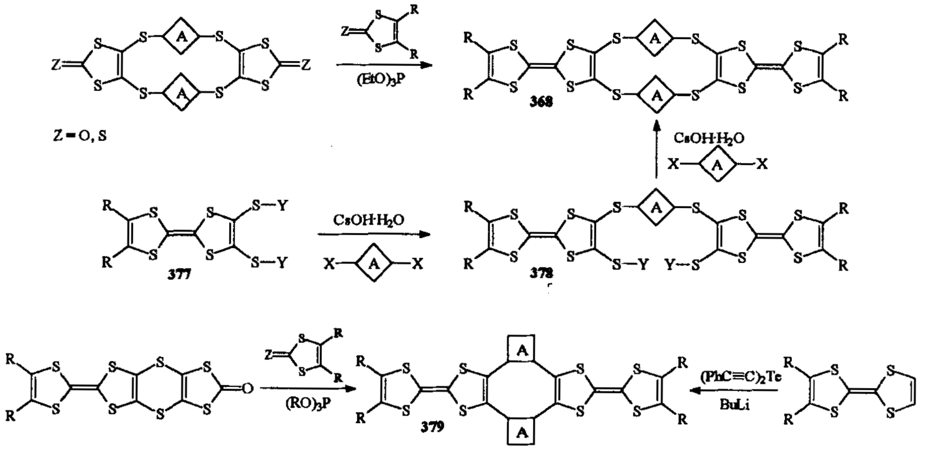
The synthesis of **369–373** provides mostly a mixture of *cis/trans* isomers, which could not be separated (see also Section 1.11).



SCHEME 192

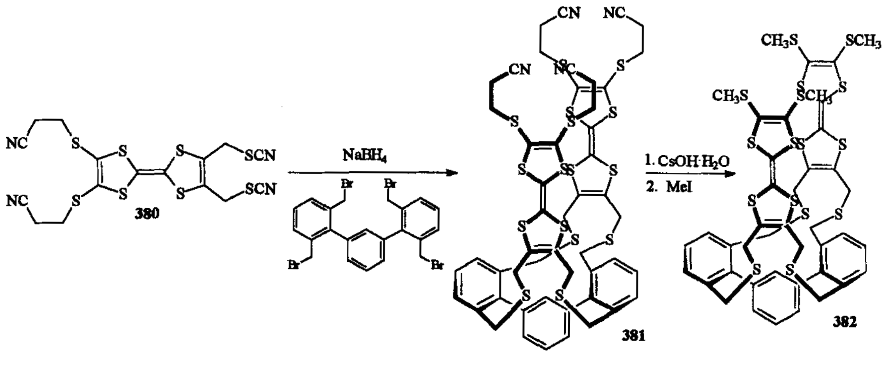
TTF dimers with single-linkage **367** are formed by different synthetic methods and the properties of these dimers also depend on the nature of the spacer. In particular, the redox properties of the TTF moiety are influenced by the kind of the spacer (conjugated or isolated linkage of the TTF moieties) or their flexibility (stretched or folded conformation). See also the discussion in Section 7.2.

Cross-coupling of bis(1,3-dithiol-2-ones) or -thiones and 1,3-dithiol-2-ones or -thiones with triethyl phosphite and subsequent purification by column chromatography provides TTF dimers **368** [760,795]. Better yields and TTF dimers **368** in purer form are prepared in a stepwise procedure by selective monodeprotection of TTF **377** ($Y = CH_2CH_2CN$) by one equivalent of cesium hydroxide. Then two of the resulting TTF monothiolates are combined with bisalkylating reagents to afford the TTF dimers **378**. Further deprotection of the TTF dimers **378** followed by cyclization with bisalkylating reagents under high-dilution conditions gave TTF dimers **368** [354,751,794,796]. This stepwise procedure enables introduction of two different links [794,797]. TTF dimers **379** linked only by two heteroatom bridges ($A = S$ or Te) are prepared by cross-coupling of the corresponding 1,3-dithiol-2-ones and -thiones with trialkyl phosphite [798–800] or in a one-pot synthesis by lithiation of the corresponding TTF derivative and subsequent reaction with bis(phenylethynyl)telluride [656,657].



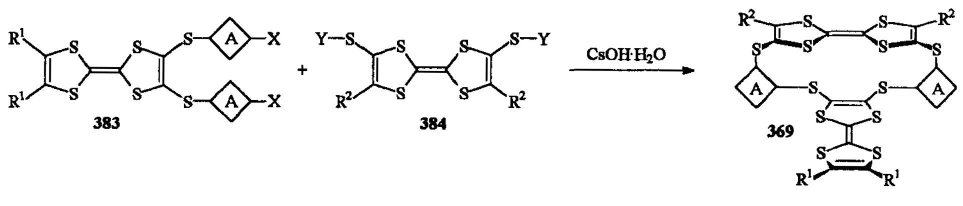
SCHEME 193

A double-linkaged TTF **368** is formed, where the two bridging groups are connected with each other based on the *m*-terphenyl framework. Deprotection of thiocyanatomethyl groups in **380** and realkylation with tetrakis(bromomethyl)terphenyl provides a 'cuppedophane' **381** which can be converted into **382** [801].



SCHEME 194

TTF **384** is deprotected with two equivalents of cesium hydroxide and affords by treatment with the bishalide **383** under high-dilution conditions TTF dimers **369** [359,364,365,802].



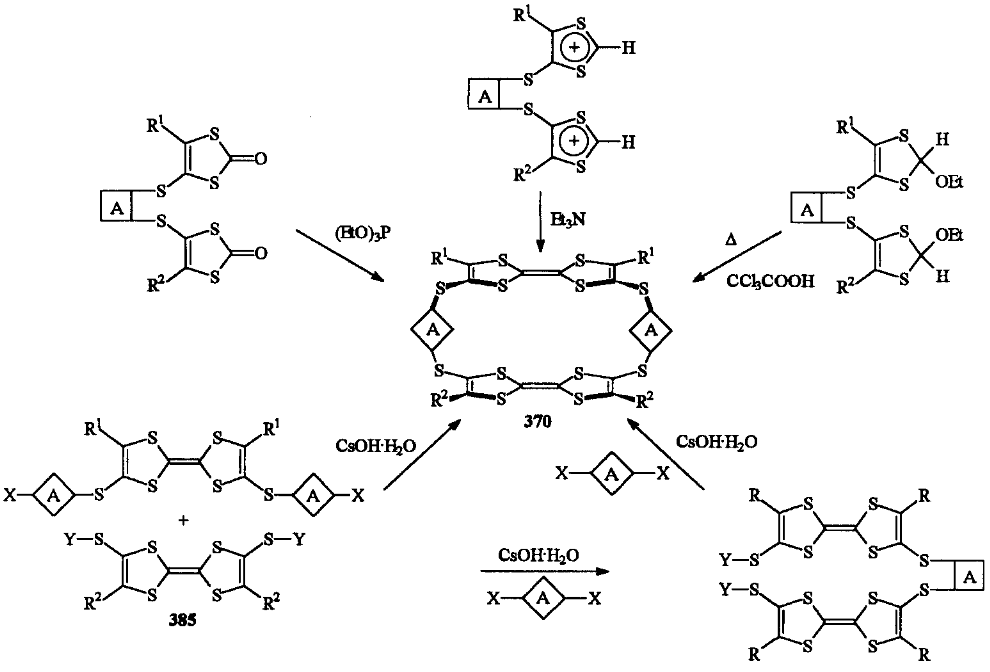
SCHEME 195

The intermolecular coupling of bis(1,3-dithiol-2-ones) [357,615,803,804], bis(2-ethoxy-1,3-dithioles) or bis(2*H*-1,3-dithiolium) salts [805,806] provides TTF dimers **370**. The corresponding tetraselenafulvalenes are also prepared by intermolecular coupling of 1,3-diselenole-2-selones [807].

After deprotection of the TTF **385** ($Y = CH_2CH_2CN$) with cesium hydroxide the dithiolate is alkylated with dihalides and the TTF dimers **370** are formed [354,365,780]. This reaction can be also performed as two-step synthesis [348,808].

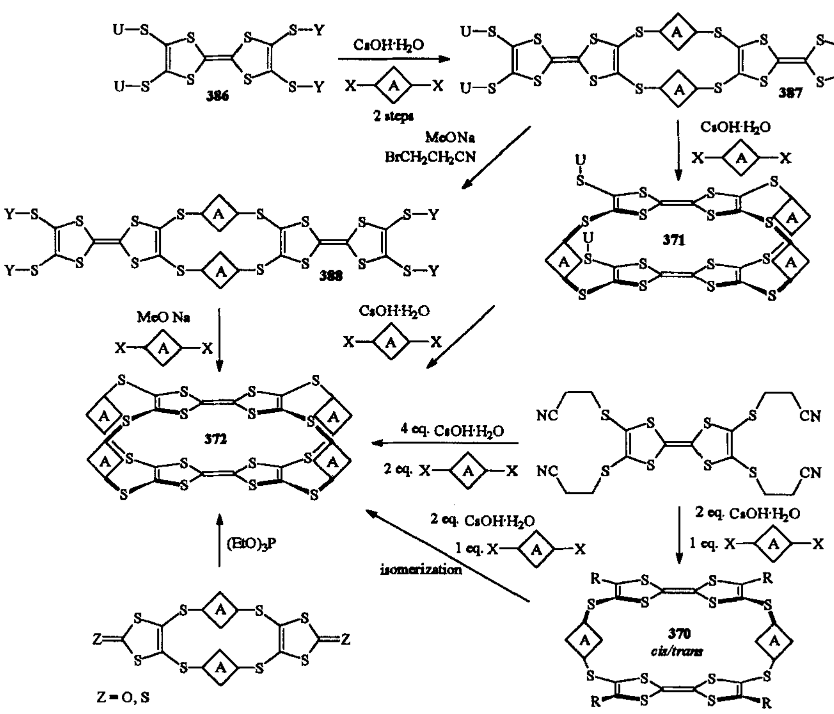
In the same way, by deprotection of the corresponding TSF ($Y = CH_2CH_2COOCH_3$) with cesium hydroxide, the dithiolate affords with alkylenedibromides the TSF dimers [358].

The TTF dimers **370** are formed and not the monomacrocycles **362**, if the length of the spacer group is considerably shorter than the thiolate–thiolate distance on 4- and 4′(5′)-position in the TTF moiety [354].



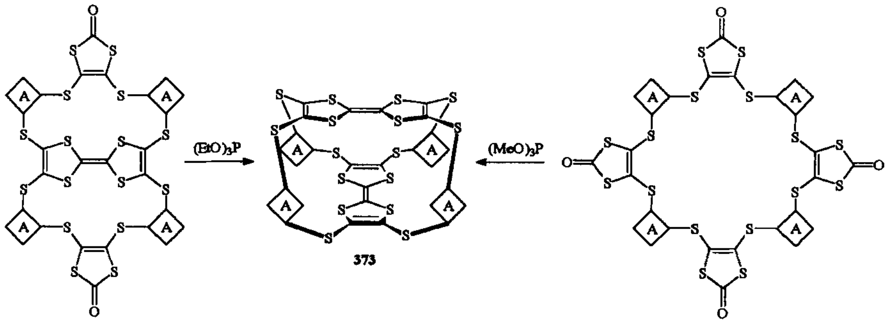
SCHEME 196

Quadruple-bridged TTF derivatives **372** are prepared by intermolecular coupling of bis(1,3-dithiol-2-ones) or -thiones [772,809]. They are also formed in a four-step deprotection/alkylation reaction of a protected TTF **386** with two different protecting groups ($U = CH_2CH_2C_6H_4NO_2$-4, $Y = CH_2CH_2CN$). As isolable intermediates triple-bridged TTF derivatives of type **371** [751] are formed. A more efficient quadruple-bridged TTF **372** is formed by an interchange of protecting groups in **387** (substitution of 4-nitrophenylethyl by cyanoethyl) and subsequent deprotection of **388** with base and realkylation with bishalide. **372** is also formed by sequential deprotection/realkylation steps of tetrakis(2-cyanoethylthio)TTF without intermediate purifications. Deprotection of tetrakis(2-cyanoethylthio)TTF with two equivalents of cesium hydroxide and realkylation with one equivalent of bishalide affords a dimer of type **370** as a mixture of *cis/trans* isomers, which is isomerized by addition of catalytic amounts of trifluoroacetic acid to a stable isomer, probably the *cis,cis*-isomer, because subsequent deprotection with further two equivalents of cesium hydroxide and realkylation with one equivalent bishalide forms the TTF **372**. Deprotection of all four thiolate functions simultaneously and realkylation with two equivalents bishalide provides **372** in lower yields and the quadruple-bridged TTF **373** as by-product [794].



SCHEME 197

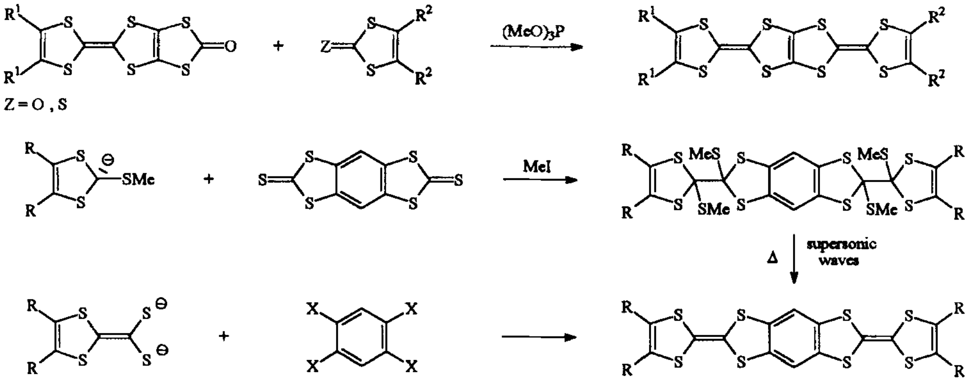
Quadruple-bridged TTF derivatives **373** with criss-cross overlapping of the two TTF moieties are synthesized by intramolecular coupling of bismacrocycles with bis(1,3-dithiol-2-one) structure [778,791,792] or in one-step by intramolecular coupling of cyclic tetramers of alkylated 1,3-dithiol-2-one-4,5-dithiolates [810,811].



SCHEME 198

Condensed types **374** of TTF dimers are formed by cross-coupling of 1,3-dithiol-2-ones, annelated with TTF framework, and 1,3-dithiol-2-ones [812] or -thiones [165,166,337,586,813–820].

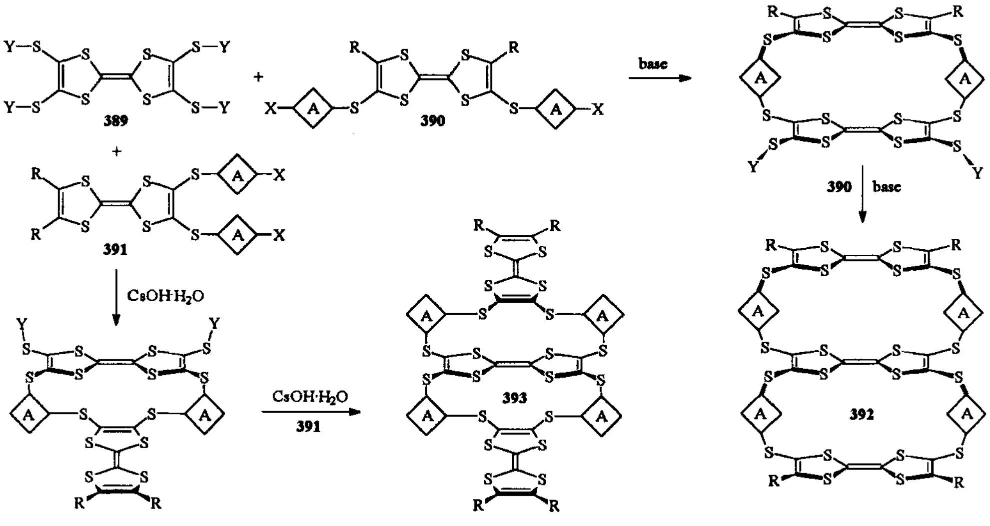
The condensed linear **375** or angular TTF dimers **376** are prepared by nucleophilic aromatic substitution by geminal dithiolates [609] or thermolysis of bis(orthothio-oxalates) [298,300–303,344,345,821].



SCHEME 199

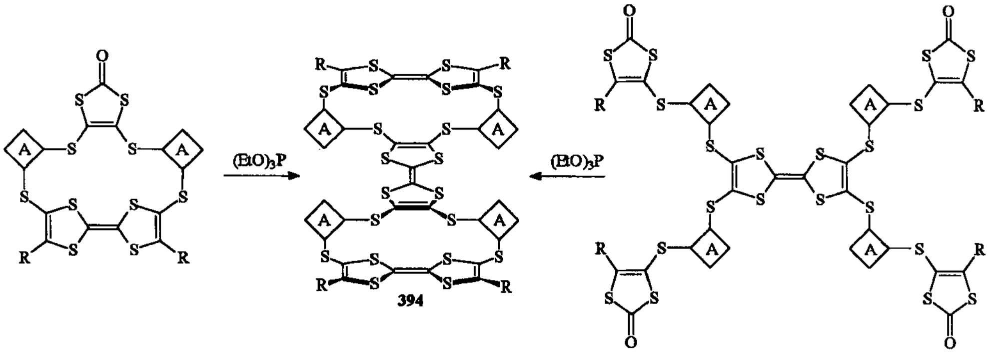
7.1.3. *Formation of TTF Tri-, Tetra-, and Pentamers*

In a stepwise deprotection of TTF **389** with cesium hydroxide ($Y = CH_2CH_2CN$ [364,365]) or potassium *t*-butoxide ($Y = CH_2CH_2COOCH_3$ [780]) and alkylation with different TTF dihalides **390** or **391** the TTF trimers **392** with connection of the TTF moieties in 4,4′(5′)-position (*ribbon* compounds) or **393** with connection of the TTF moieties in 4,4′(5′)- and 4,5-position are synthesized.



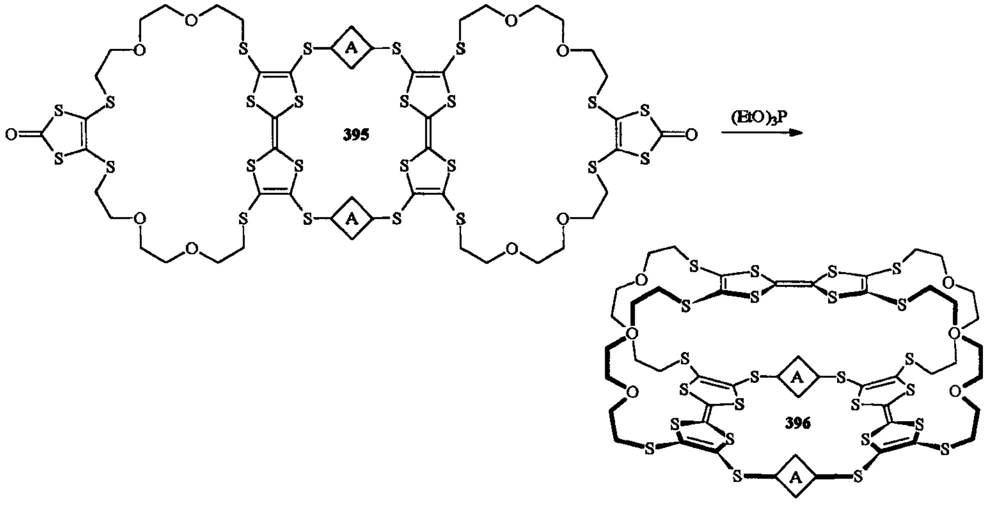
SCHEME 200

Intermolecular or intramolecular coupling of 1,3-dithiol-2-one derivatives with triethyl phosphite provides TTF trimers **394** with connection of the TTF moieties in 4,5- and 4,4′(5′)-position [365,780].



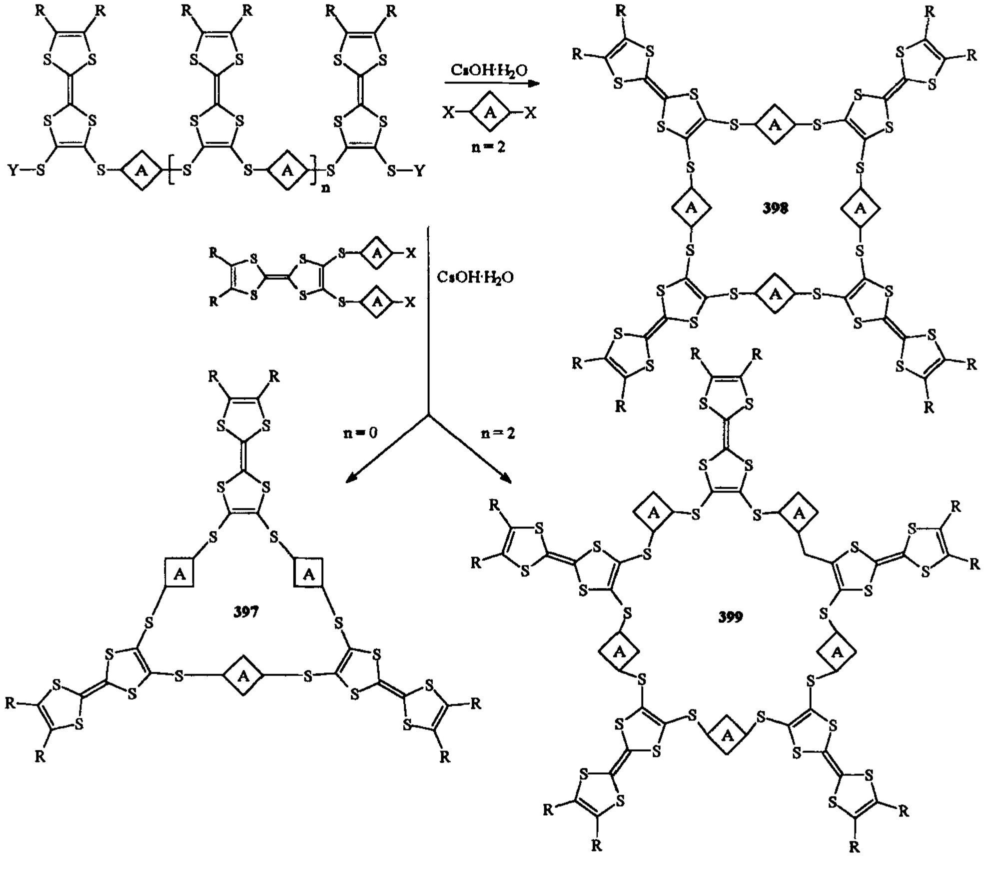
SCHEME 201

Intramolecular coupling of 1,3-dithiol-2-one derivatives of a TTF dimer **395** with triethyl phosphite affords TTF trimers **396**, where a large cavity is created by the TTF pair and the third TTF unit which is separated from this pair by long and flexible bis(ethoxy)ethyl linkers [808].



SCHEME 202

TTF-macrocycles **397–399** with three, four, or five TTF moieties connected in 4,5-position are formed by analogous deprotection/alkylation reactions (Y = CH_2CH_2CN) [822], where by using of two different TTF derivatives cyclic trimeric TTF **397** are prepared with different substituents R [797].



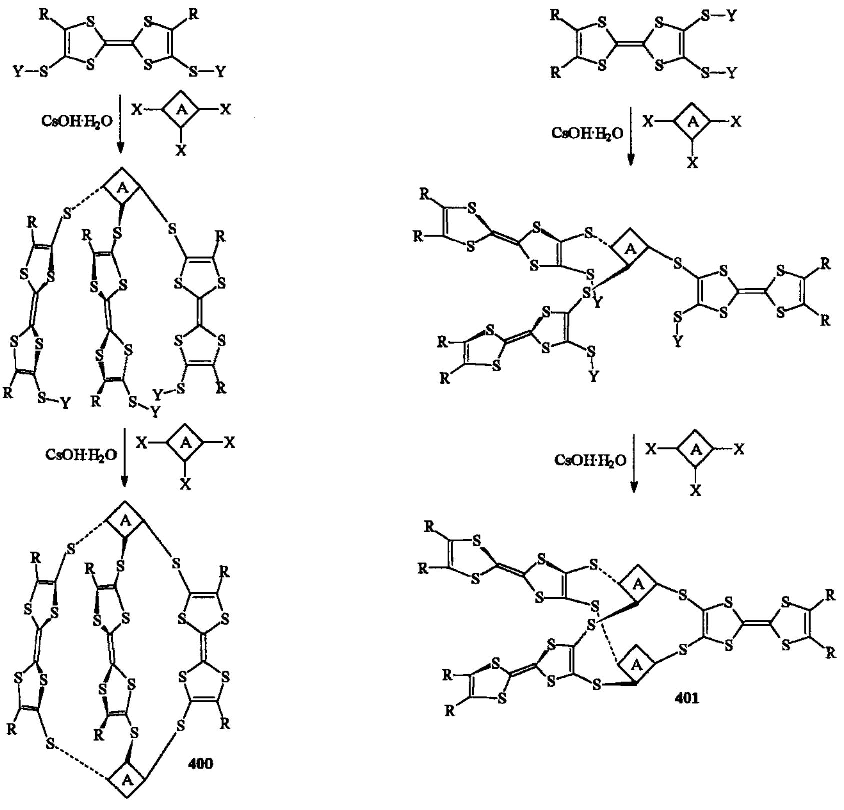
SCHEME 203

A 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivative with a hydroxymethyl group in the 4-position of the TTF unit yields with 1, 3, 5-benzenetricarbonyl trichloride a trimer [823].

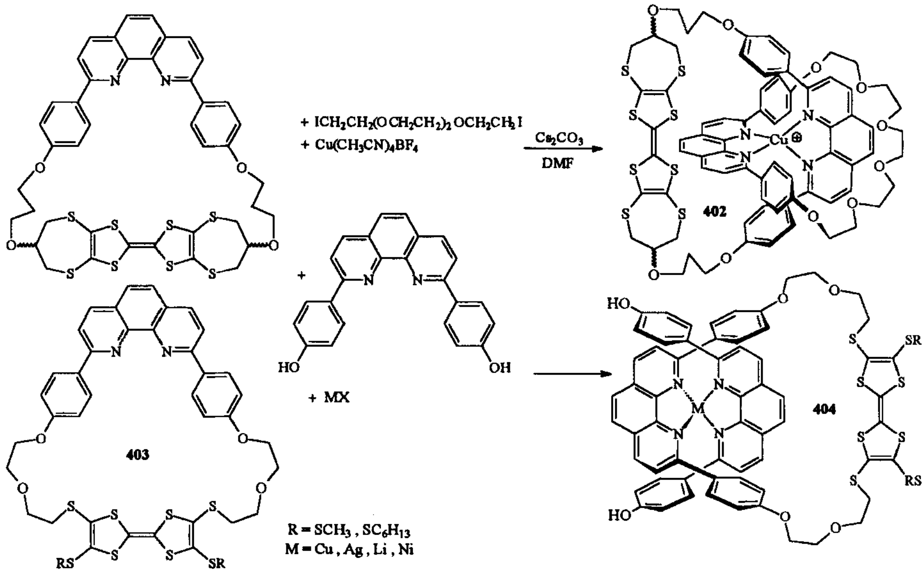
TTF trimers **400** and **401** connected by two bridges with three valencies are synthesized in a two-step deprotection–alkylation reaction, where the second step is accomplished under high-dilution conditions ($Y = CH_2CH_2CN$) [360,361].

7.1.4. Formation of Catenanes and Rotaxanes

Firstly the catenane **402** with additional copper coordination is prepared by reaction of a TTF monomacrocycle with 2,9-di(4-hydroxyphenyl)-1,10-phenanthroline, the diiodo derivative of pentaethyleneglycol and copper(I)tetrafluoroborate [824]. The related 4,4′(5′) macrocycle-substituted TTF **403** forms with 2,9-di(4-hydroxyphenyl)-1,10-phenanthroline and metal ions the corresponding precatenate complexes **404**. Also a 4,5-macrocycle-substituted TTF affords in the same way a precatenate complex [781].



SCHEME 204

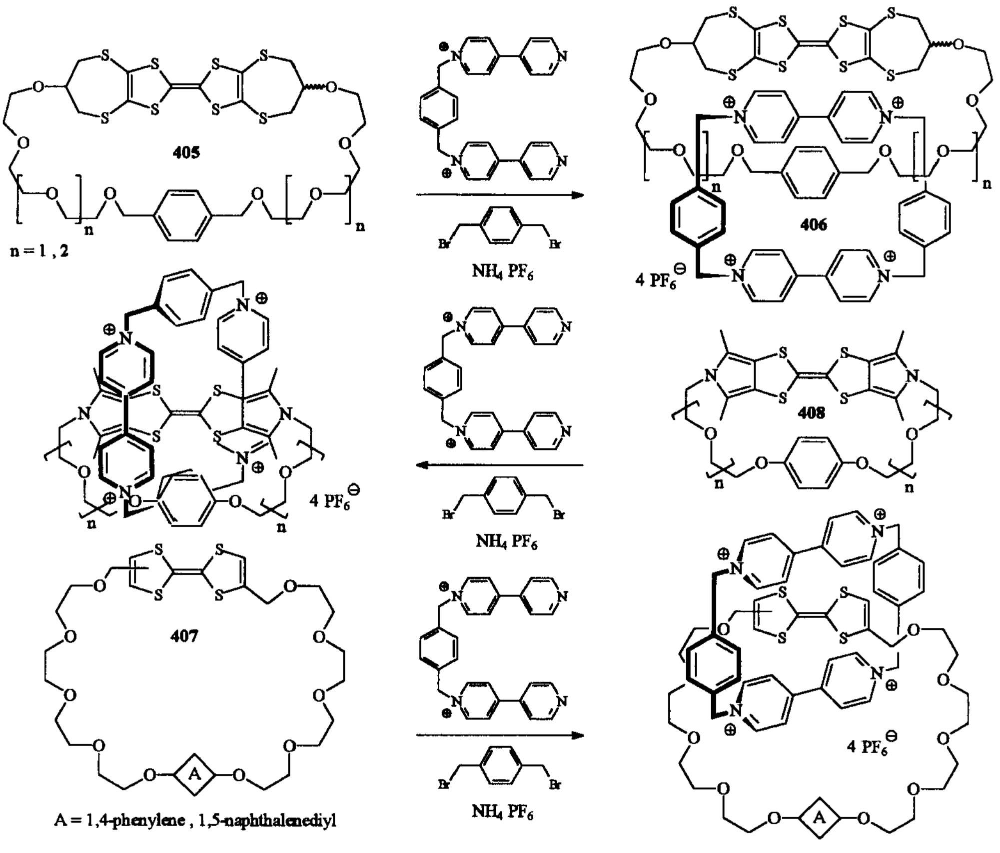


SCHEME 205

The analogous TTF monomacrocycles **405** yield with 1,4-bis(bromomethyl)benzene and 1,1′-[1,4-phenylenebis(methylene)]-bis-(4,4′-bipyridinium) bis(hexafluorophosphate) catenanes **406** threading in the solid state the 1,4-phenylene ring of the polyether through the center of the paraquat, while the TTF moiety resides alongside, confirmed by X-ray crystallographic analysis [825].

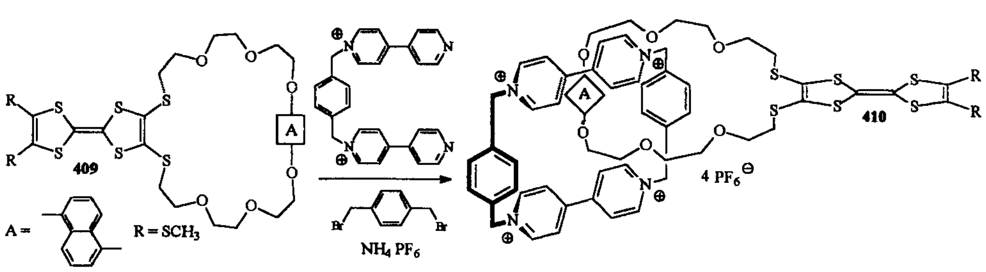
In the case of the TTF **407** the TTF moiety occupies the cavity of the tetracationic acceptor, since the TTF unit is a stronger donor than 1,4-dioxybenzene or 1,5-dioxynaphthalene [362,826].

^{1}H NMR and UV–Vis spectroscopic investigations of catenanes between pyrrolo-annelated TTF macrocycles **408** containing 1,4-dioxybenzene units and cyclobis(paraquat-1,4-phenylene) show that in the case of the smallest catenane ($n = 1$) only the TTF unit is encircled by cyclobis(paraquat-1,4-phenylene) and in the case of $n = 2$ or $n = 3$, the TTF unit as well as the 1,4-dioxybenzene unit is encircled with greater extent of the latter [782].



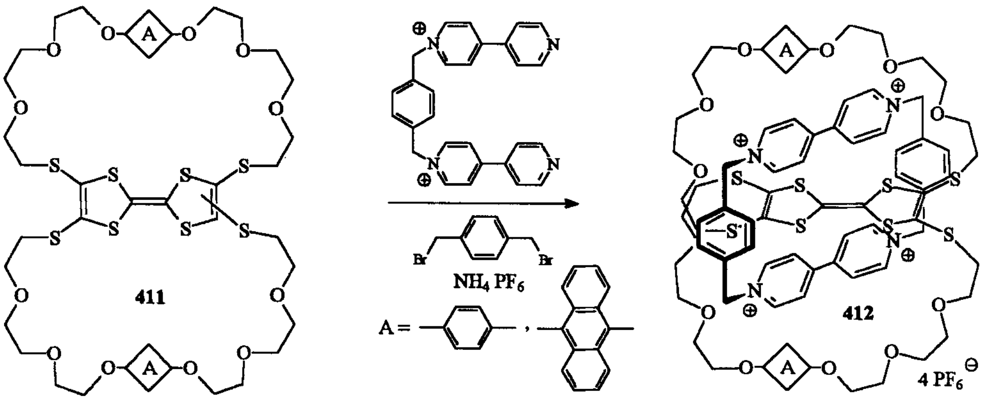
SCHEME 206

Reaction of monomacrocycles **409** with 1,4-bis(bromomethyl)benzene and 1,1′-[1,4-phenylenebis(methylene)]bis-(4,4′-bipyridinium) bis(hexafluorophosphate) provides catenanes **410**, respectively [365]. Due to the negative volume of activation for such reactions, the formation of catenanes is facilitated by ultra-high pressure.



SCHEME 207

In a similar reaction of TTF bismacrocycles with 1,4-bis(bromomethyl)benzene and 1,1′-[1,4-phenylenebis(methylene)]bis-(4,4′-bipyridinium) bis(hexafluorophosphate) further catenanes are prepared. The TTF **411** affords depending on the nature of the linker A, besides the catenane **412** (with *trans*-**411**), further catenanes, the analogue catenane with *cis*-**411**, a catenane concatenating a polyether cycle with the paraquat cycle and a catenane concatenating the two polyether cycles with one paraquat cycle, respectively [362,363].

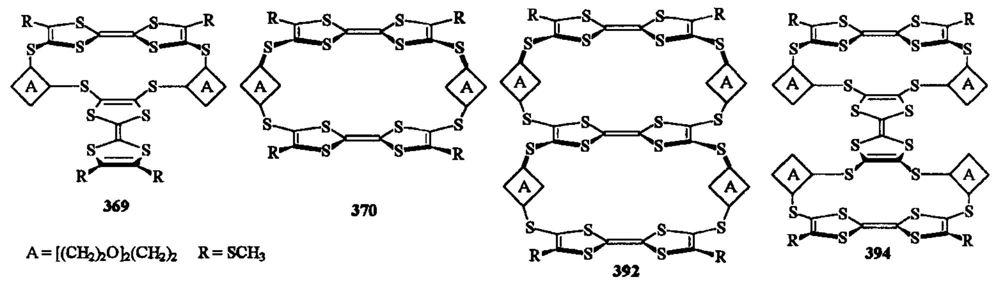


SCHEME 208

By using two tetrafluorophenylene units as linking groups in the tetracationic cyclophane acceptor no catenane was generated, in which the two polyether cycles were encircled by tetracationic cyclophanes (A = 1,5-naphthalenediyl). The tetracationic cyclophane prefers to encircle around the TTF subunit [366].

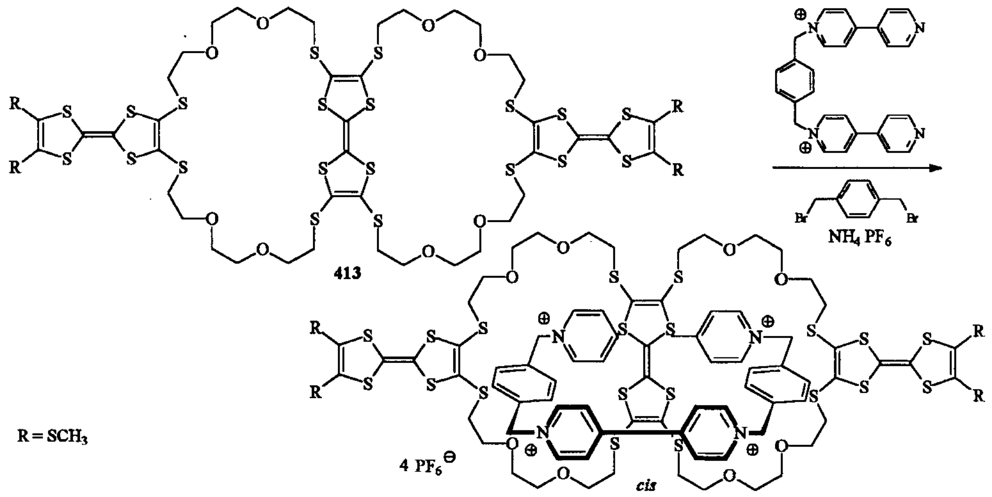
The TTF dimers **369** and **370** or trimers **392** and **394** form with 1,4-bis(bromomethyl)benzene and 1,1′-[1,4-phenylenebis-(methylene)]bis(4,4′-bipyridinium) bis(hexafluorophosphate) different catenanes as *cis*/*trans* mixtures [365].

Starting from TTF trimer **413**, 1,4-bis(bromomethyl)benzene and 1,1′-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridinium) bis(hexafluorophosphate) a *cis* catenane could be generated exclusively due to the donor–acceptor interactions between two peripheral TTF-donors and the bipyridinium acceptors. In solution, even in the presence of trifluoroacetic acid, no isomerization is observed [364,365].



A = $[(CH_2)_2O]_2(CH_2)_2$ R = SCH_3

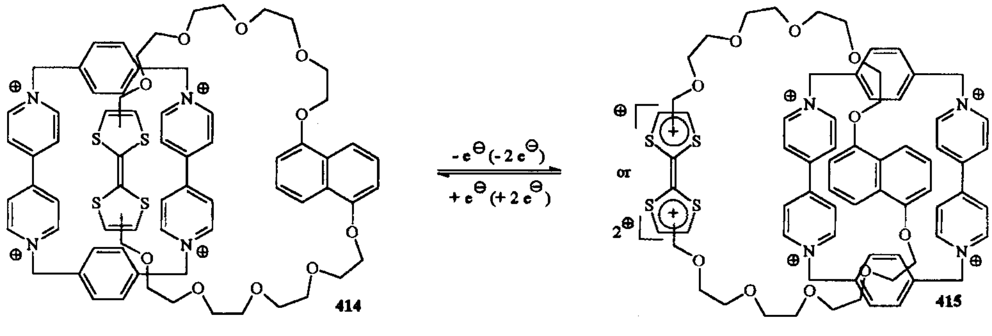
SCHEME 209



R = SCH_3

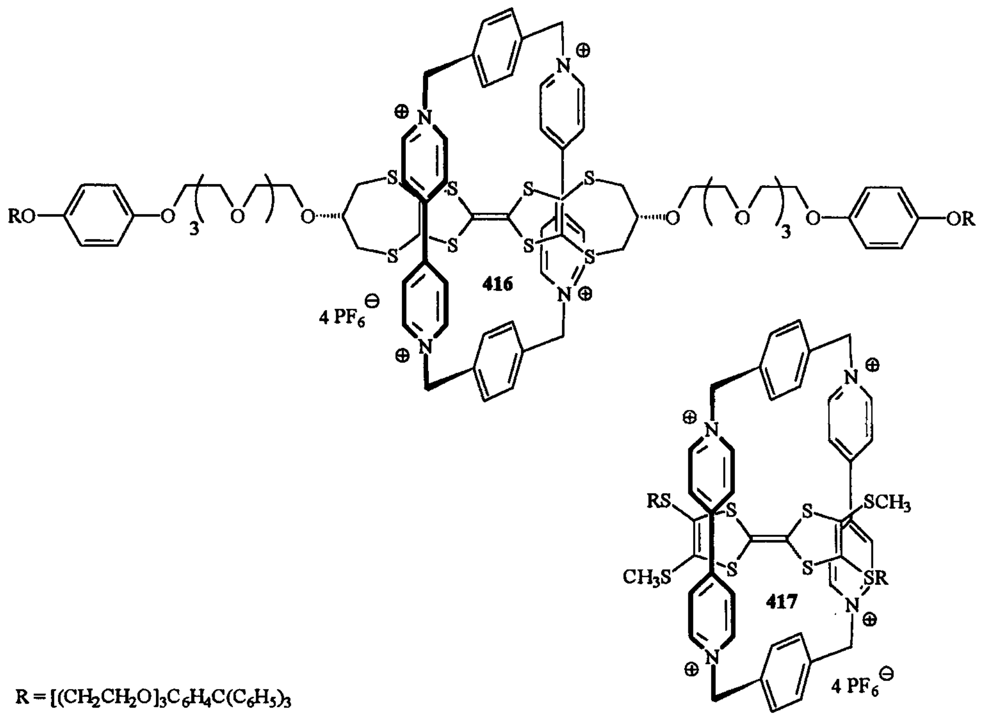
SCHEME 210

By chemical or electrochemical redox reactions a reversible switching between the two [2]catenanes **414** and **415** is observed. In the reduced state the tetracationic cyclophane acceptor encircles the TTF subunit and in the oxidized state (mono- or dioxidized) the 1,5-naphthalenedioxy subunit. The redox switching is accompanied by a colour change and can be followed by ^1H NMR-, UV–Vis-, or cyclovoltammetry measurements [783].



SCHEME 211

Tetrathiafulvalenes with long chain substituents and stoppers at the end of the substituents afford rotaxanes **416** [827] and **417** [362] with cyclobis(paraquat-1,4-phenylene). For the rotaxane **416** ^{1}H NMR and UV–Vis spectroscopic studies show that in acetone the tetracationic cyclophane occupies exclusively the two equivalent hydroquinone rings, whilst in DMSO the cyclophane is located predominantly on the TTF unit resulting two translational isomers. After electrochemical oxidation of the TTF moiety to the radical cation the decreased donor strength of the TTF unit increases the energy barrier to the passage of the cyclophane along the thread causing the cyclophane to be effectively tethered at a hydroquinone unit [827,828]. Rotaxane **417** is isolated as a mixture of *cis*- and *trans*-isomers, which could not be separated. The tetracationic cycle is not fixed and can move between the two triphenylmethylphenyl stoppers so that the TTF moiety can isomerize.



416

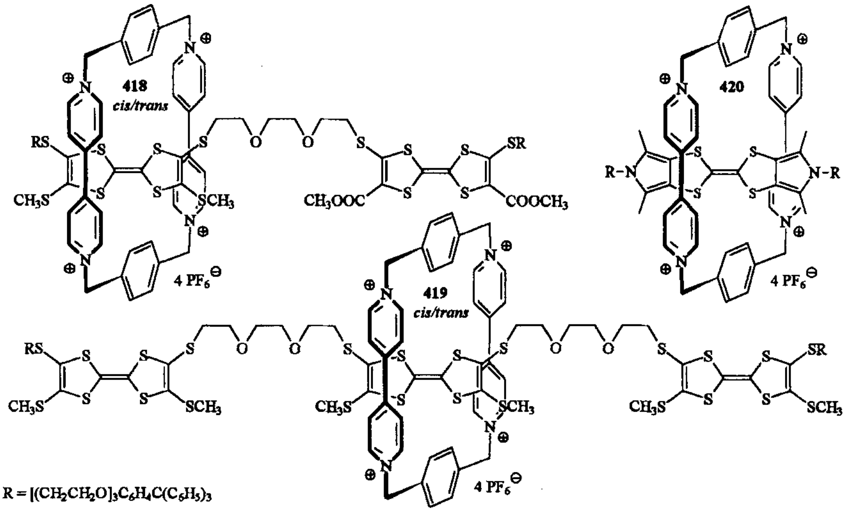
417

$R = [(CH_2CH_2O]_3C_6H_4C(C_6H_5)_3$

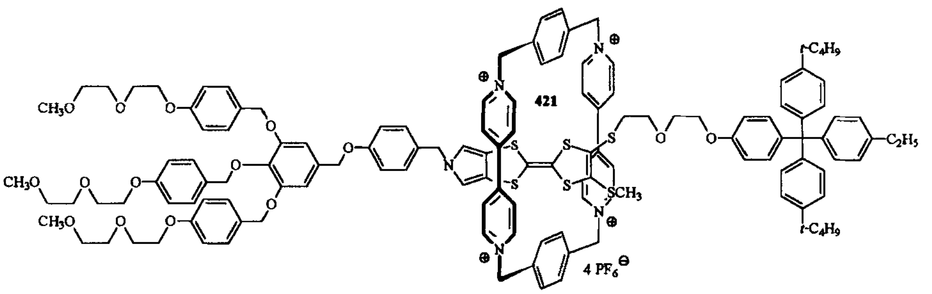
SCHEME 212

In a stepwise deprotection/realkylation reaction involving a TTF derivative with two different thiolate protecting groups a linear TTF dimer with two different substituted TTF units and a linear TTF trimer are prepared which form with cyclobis(paraquat-1,4-phenylene) the corresponding rotaxanes **418** and **419** as *cis*/*trans* mixture. In the rotaxane **418** either the diester TTF or the tetramercapto TTF is encircled in a ratio of 8 : 10. The pyrrolo TTF rotaxane **420** forms no isomers [829].

An asymmetric TTF with one hydrophilic and one hydrophobic stopper provides by encircling with cyclobis(paraquat-1,4-phenylene), a rotaxane **421** with two different stoppers [830].

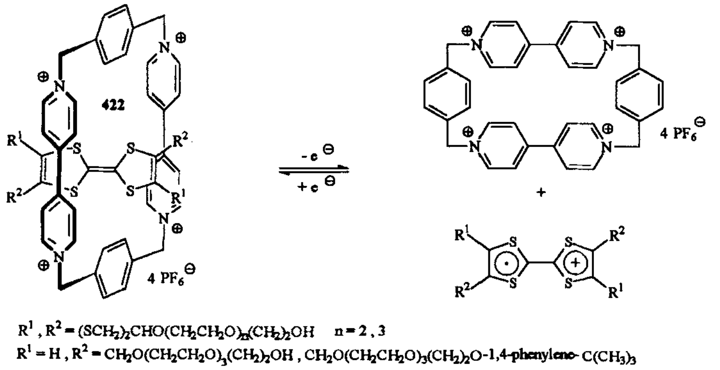


SCHEME 213



SCHEME 214

Upon mixing of equimolar amounts of TTF derivatives and cyclobis(paraquat-1,4-phenylene) the pseudorotaxanes **422** are formed. Electrochemical oxidation of the TTF derivative to the monocation leads to the dissociation into their separate components as a result of disruption of the CT interaction and electrostatic repulsion between the two positively charged components. Reduction of the TTF monocation to the neutral state is accompanied by the formation of the pseudorotaxane [825,826,831].

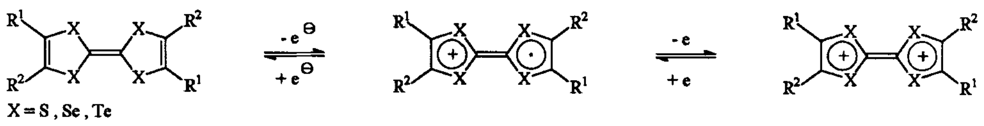


SCHEME 215

7.2. Redox Reactions and Spectroscopic Behaviour of Tetrathia-, Tetraselena-, and Tetratellurafulvalenes

7.2.1. Redox Reactions

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



SCHEME 216

Polarographically it has been proven that these electron transfers are reversible for the tetrathia- [189,832] as well as for the tetraselena- [833] and tetratellurafulvalenes [431].

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 I).

This is caused by two 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 TTF should primarily involve the π-bonded network and in TTeF the tellurium lone pairs [431,432].

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

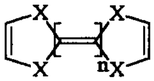
TABLE I Oxidation potentials of substituted tetrathia-, tetraselena-, and tetratellurafulvalenes (*vs.* sce) [431,432]

Compound	E_1^{Ox} [V]	E_2^{Ox} [V]	ΔE [V]
	0.24^a	0.73	0.49
	0.42^a	0.81	0.39
	0.40^a	0.69	0.29
	0.71^b	1.14	0.43
	0.78^b	1.17	0.39
	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 [98,834].

[b] dichloromethane, 0.2 M By_4NBF_4, TMTTF, HMTTF: tetramethyl-, hexamethylene tetrathiafulvalene, respectively; TMTSF, HMTSF: tetramethyl-, hexamethylenetetraselenafulvalene, respectively, HMTTeF: hexamethylenetellurafulvalene, DBTTF, DBTSF, DBTTeF: dibenzotetrathia-, dibenzotetraselena-, dibenzotetratellurafulvalene, respectively.

TABLE II Oxidation potentials of vinylogous tetrathia- and tetraselenafulvalenes and their parent compounds [437,474] 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	0.22	
1	Se	0.49	0.77	0.28
2	Se	0.33	0.47	0.14

the difference is so small that only one wave, representing a two-electron oxidation, appears (Table II) [474]. However, in dichloromethane, which allows a better separation of the redox waves, two separated one-electron oxidation peaks with very weak values of ΔE are observed [477].

As mentioned above and demonstrated in Tables I and II, TTF derivatives with an extended π-system between the two 1,3-dithiole moieties are mostly stronger donors than the parent TTF. The donor ability is increased by cumulenic and quinoid structures (Table III). In the last case the two single-electron redox waves coalesce to a single, two-electron redox wave. This means that in the radical cation and dication states of these donors the one-site Coulomb repulsion is greatly reduced. In a dimeric TTF with 1,4-quinodimethane structure only one wave corresponding to a four-electron transfer is observed [835]. However, irreversible redox reactions indicate that cumulenic TTF are unsuitable donors for the preparation of organic conductors because of the extreme instability of the neutral species, radical cations or dications.

The donor strength is also influenced by substituents. It is increased by electron-donating and lowered by electron-withdrawing substituents. In substituted TTF with the same kind of substituents, such as diaryl substituted TTF, the first half-wave potential correlates better with the Hammett σ_p^+ values ($R = 0.94$) than with the σ_p values ($R = 0.91$) (Fig. 1) [836].

Also the oxidation potential of the two-electron transfer for diaryl substituted vinylogues tetrathiafulvalenes provides a good correlation ($R = 0.994$) with the σ_p^+ substituent constants (Fig. 2) [462].

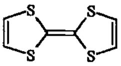
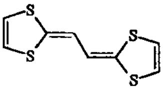
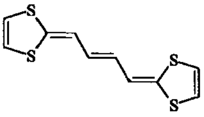
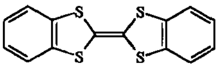
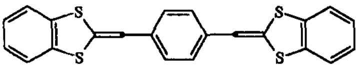
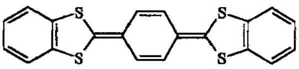
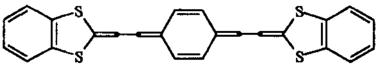
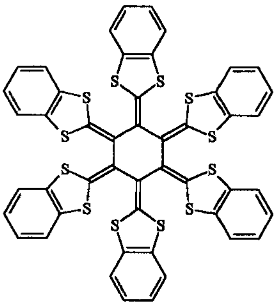
However, in the case of sulfur and seleno substituted TTF, a good correlation ($R = 0.99$) between the first half-wave potential and the sum of σ_m of each substituent on the TTF core is obtained (Fig. 3) [152].

Also in the case of multisubstituted TTF a better correlation between the first half-wave potential and inductive parameter ($\Sigma\sigma_m$, $R = 0.99$) than mesomeric parameter (σ_p^+, $R = 0.78$) is founded (Fig. 4) [837].

If two or three TTF moieties are connected, the corresponding 'dimeric' or 'trimeric' TTF should be able to donate four or six electrons, respectively. Depending on the kind of connection between the TTF moieties (every TTF unit bears the same substituents) one can find in the cyclic voltammogram of 'dimeric' TTF two, three, or four redox couples [47].

Group 1 The TTF moieties are conjugatively bridged or annelated to form a new donor with extension of the π-system. In this case the oxidation can take place in

TABLE III Oxidation potentials of vinylogous, cumulenic, acetylenic, and quinoid tetrathiafulvalenes in acetonitrile (*vs.* Ag/AgCl electrode, 0.1 M Et_4NClO_4 or 0.1 M Bu_4NClO_4)

Compound	E_1^{Ox} [V]	E_2^{Ox} [V]	*References*
	0.34	0.71	463
	0.20	0.36	463
	0.22	0.22	463
	(0.07)	(0.31)[a]	482
	(−0.12)	(0.25)[a]	482
	0.72	1.06	464
	0.67	1.02[b]	480
	0.64	0.78	464
	0.27	0.27	464
	0.40	0.40	464
	0.43	(0.65)[c]	470

Parentheses indicate an irreversible redox reaction, (a) BF_4^- salts of the corresponding dications, (b) peak potentials *vs.* sce, (c) in benzonitrile.

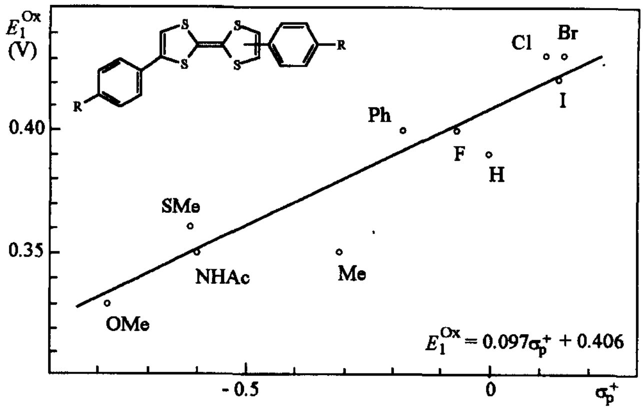


FIGURE 1 Relation of half-wave potentials *vs.* sce for oxidation of 2,6(7)-diaryl substituted TTF in methanol/benzene (4 : 1, v : v) to Hammett substituent constants.

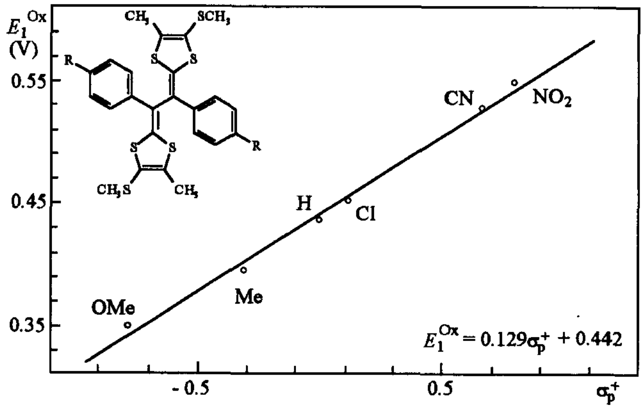
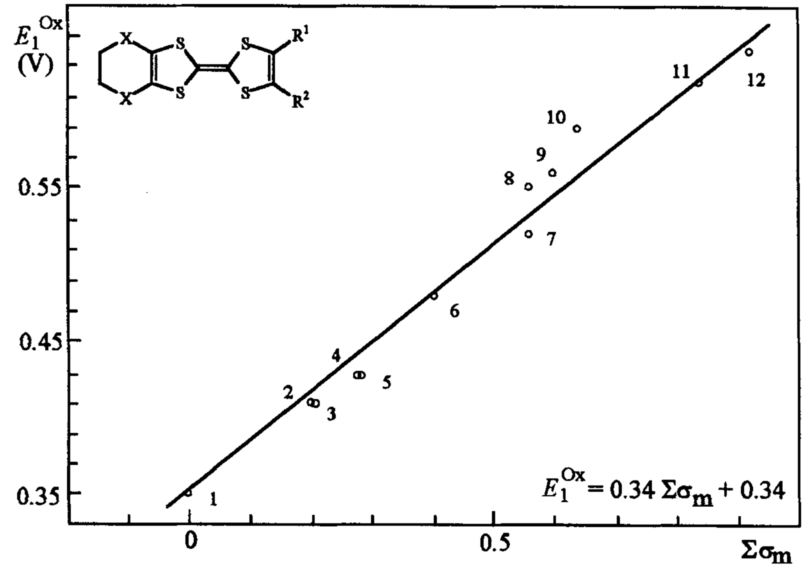


FIGURE 2 Relation of half-wave potentials *vs.* sce for oxidation of diaryl substituted vinylogues TTF in acetonitrile to Hammett substituent constants.

four one-electron steps. These four waves in the cyclic voltammetry correspond to the oxidation to the mono-, di-, tri-, and tetracation. The 'trimeric' TTF provides six one-electron oxidation waves (Table IV).

Group 2 The TTF moieties are linked by a bridging group, which provides a conjugation between the TTF subunits, but there is no coplanarity between the TTF subunits and the bridging group. These dimers or trimers show two redox waves due to simultaneous oxidation of the two or three TTF units at the same potential (two two-electron or two three-electron oxidation waves). There is no interaction between the TTF units (Table V).

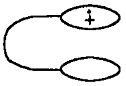
Group 3 The TTF moieties are linked by a spacer group, with the individual TTF units electronically isolated, but the arrangement of the TTF units enables a Coulomb interaction through space. Such dimers provide, by oxidation, three waves in the cyclic voltammogram. The 'sandwich' structure of the dimer lowers the first oxidation potential by interaction of the two TTF π-systems, resulting in stabilization of the mono radical cation. At slightly higher potential the second electron is removed. As a result of the Coulomb repulsion between the two positively charged TTF subunits



	R^1	R^2	X		R^1	R^2	X
1	Ttf			7	$S(CH_2)_2S$		S
2	H	H	Se	8	CHO	H	Se
3	CH_2OH	H	Se	9	$COOCH_3$	H	S
4	H	H	S	10	CHO	H	S
5	CH_2OH	H	S	11	$COOCH_3$	$COOCH_3$	Se
6	$Se(CH_2)_2Se$		Se	12	$COOCH_3$	$COOCH_3$	S

FIGURE 3 Relation of half-wave potentials *vs.* Ag/AgCl for oxidation of ethylenedithio and ethylenediselene substituted TTF in acetonitrile to Hammett substituent constants.

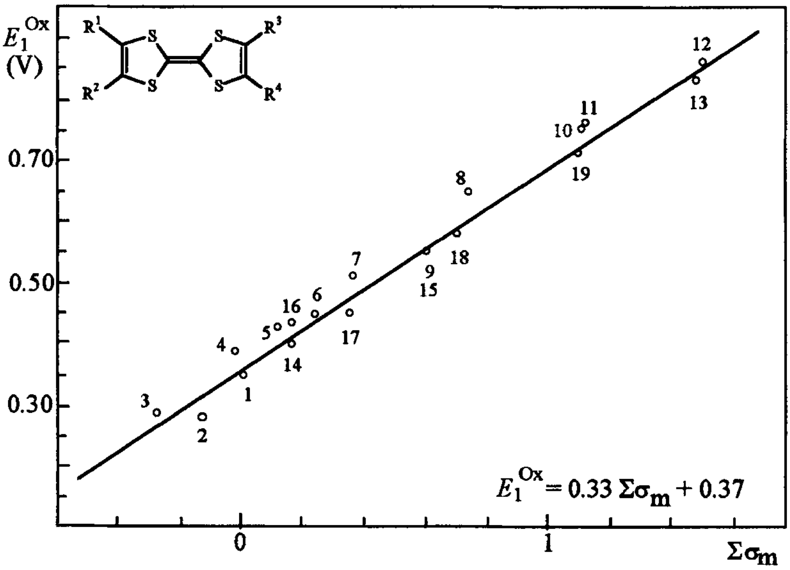
in the dimer, the two TTF subunits unfold. The two TTF units now behave like individual molecules and the third and fourth electrons are removed at the same potential. By the same token in tris(tetrathiafulvalenyl)phosphine three close-lying one-electron oxidation waves are observed, followed by a three-electron wave (Table VI) [640].



SCHEME 217

Such electronic interaction is also observed in a series of tetrathiafulvalene substituted polystyrenes [838–841] or tetrathiafulvalene derivatized polythiophene [842]. The first wave in the cyclic voltammogram is broadened considerably relative to the ideal case and close inspection reveals that this wave is a superposition of two waves. The formation of the mixed-valence dimer $(TTF)_2^+$ is confirmed by spectroscopic measurements.

Group 4 The TTF moieties are linked by spacer groups and there is no interaction between the TTF units. The individual TTF units are sterically and electronically



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
1	H	H	H	H	11	$COCH_3$	$COOC_4H_9$	$COOC_4H_9$	H
2	CH_3	CH_3	H	H	12	$COCH_3$	$COOC_4H_9$	$COOC_4H_9$	$COCH_3$
3	CH_3	CH_3	CH_3	CH_3	13	$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$
4	CH_3	CH_3	C_6H_5	C_6H_5	14	SCH_3	SCH_3	CH_3	CH_3
5	C_6H_5	H	C_6H_5	H	15	SCH_3	SCH_3	SCH_3	SCH_3
6	C_6H_5	C_6H_5	C_6H_5	C_6H_5	16	SCH_3	C_2H_5	SCH_3	C_2H_5
7	$COOC_4H_9$	H	H	H	17	I	H	H	H
8	$COOC_4H_9$	H	$COOC_4H_9$	H	18	I	H	I	H
9	$COOCH_3$	$COOCH_3$	CH_3	CH_3	19	I	$COOC_4H_9$	$COOC_4H_9$	H
10	$COOC_4H_9$	$COOC_2H_5$	$COOC_4H_9$	H					

FIGURE 4 Relation of half-wave potentials *vs.* sce for oxidation of multi-substituted TTF in acetonitrile to Hammett substituent constants.

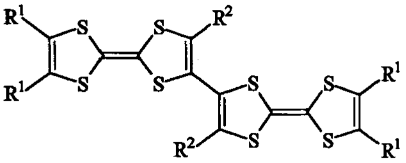
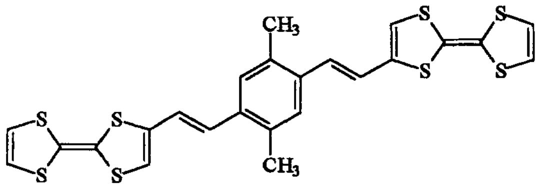
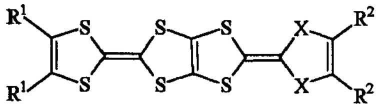
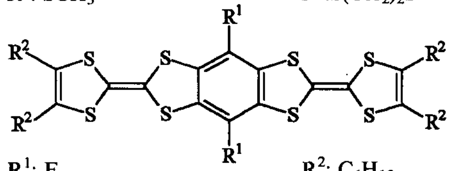
isolated. In such dimers or trimers the TTF units are oxidized at the same potential and only two two-electron or two three-electron oxidation waves are seen, respectively (Table VII).

SCHEME 218

Sometimes in polar solvents in Group 1 or Group 3 dimeric TTF only a broadening of the oxidation wave is observed in the cyclic voltammogram. A change to a less polar solvent leads to separation of the waves [640,717].

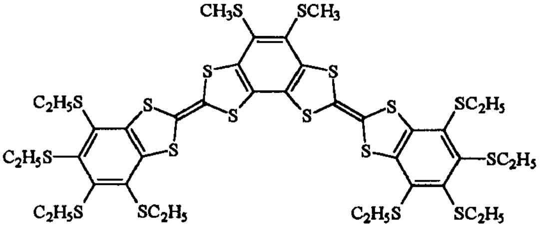
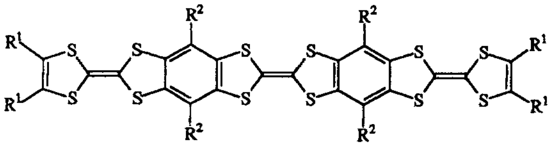
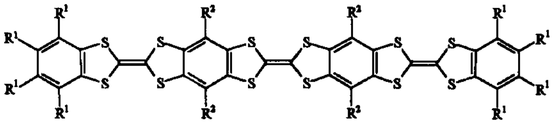
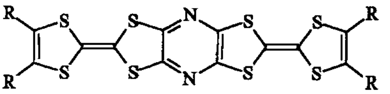
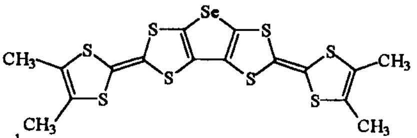
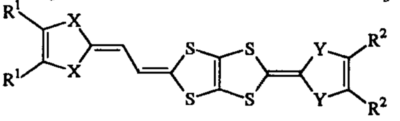
Donor properties of TTF and the reversibility of the electron transfer made TTF an interesting one-electron donor reagent or catalyst. TTF can initiate radical cyclization by transfer an electron to a diazonium cation, which leads after liberation of nitrogen to

TABLE IV Oxidation potentials of group 1 dimeric or trimeric tetrathiafulvalenes in dichloromethane (*vs*. sce, 0.1 M Bu_4NPF_6 or 0.1 M Bu_4NClO_4)

Compound			E_1^{Ox} [V]	E_2^{Ox} [V]	E_3^{Ox} [V]	E_4^{Ox} [V]	E_5^{Ox} [V]	E_6^{Ox} [V]	*References*
									
R^1: H	R^2: H		0.45	0.65	$0.97^{a,j,k}$				663, 756
R^1: SCH_3	R^2: H		0.50	0.59	0.85^{a}				843
R^1: CH_3	R^2: CH_3		0.38	0.46	0.75	$0.78^{j,k}$			664
R^1: SCH_3	R^2: CH_3		0.47	0.54	0.77^{i}				653
R^1: $S(CH_2)_2S$	R^2: CH_3		0.54	0.63	0.92^{i}				653
R^1: SCH_3	R^2:SCH_3		0.53	0.60	0.77^{i}				653
			(0.44)	(0.69)	$(0.92)^{b}$				717
			0.51	0.80^{c}					717
									
R^1: H	R^2: H	X: S	0.44	0.62	(1.05)	$(1.13)^{a}$			337
R^1: H	R^2: $(CH_2)_3$	X: S	0.43	0.67	1.01	$(1.30)^{a}$			166
R^1: H	R^2: SCH_3	X: S	0.49	0.71	0.99	$(1.13)^{a}$			813
R^1: CH_3	R^2: SCH_3	X: S	0.43	0.68	0.98	$(1.17)^{a}$			814
R^1: $(CH_2)_3$	R^2: SCH_3	X: S	0.46	0.69	0.98	$(1.13)^{a}$			844
R^1: $(CH_2)_3$	R^2: $S(CH_2)_3S$	X: S	0.46	0.65	0.90	$(1.32)^{a}$			166
R^1: $(CH_2)_3$	R^2: $COOCH_3$	X: S	0.68	0.91	1.20	$(1.68)^{i}$			166
R^1: $O(CH_2)_2O$	R^2: $O(CH_2)_2O$	X: S	0.47	0.62	(0.99)	$(1.14)^{a}$			815
R^1: SCH_3	R^2: SCH_3	X: S	0.53	0.72	0.99	1.11^{a}			165
R^1: SC_6H_{13}	R^2:SC_6H_{13}	X: S	0.65	0.81	1.08	$(1.20)^{i}$			845
R^1: SCH_3	R^2:$O(CH_2)_2S$	X: S	0.51	0.72	0.97	1.12^{a}			813
R^1: SCH_3	R^2: $S(CH_2)_2$	X: S	0.53	0.74	1.00	$(1.18)^{a}$			813
R^1: SCH_3	R^2: $COOCH_3$	X: S	0.58	0.81	1.12	$(1.31)^{a}$			813
R^1: $SeCH_3$	R^2: $SeCH_3$	X: S	0.43	0.65	0.97	$1.00^{a,j}$			816
R^1: SCH_3	R^2:$S(CH_2)_2S$	X: Se	0.49	0.66	0.90	$1.14^{a,j}$			168
									
R^1: F	R^2: C_6H_{13}		0.54	0.70	1.18	1.38			609
R^1: SC_6H_{13}	R^2: CH_3		0.39	0.61	1.07	1.23			609
R^1: OC_6H_{13}	R^2: $S(CH_2)_2S$		0.38	0.59	0.95	(1.16)			300
R^1: OC_6H_{13}	R^2: SC_6H_{13}		0.36	0.53	0.86	0.96			302
R^1:OC_2H_4Cl	R^2: SC_6H_{13}		0.41	0.56	0.90	1.00			302
R^1:SC_5H_{11}-*i*	R^2: SC_6H_{13}		0.38	0.59	0.90	1.02			846
R^1: $OCH_2C_6H_3(C_4H_9\text{-}t)_2$-3,5	R^2: $(CH{=}CH)_2$		0.46	0.68	1.13	1.29			301
R^1: SC_5H_{11}-*i*	R^2: $(CH{=}CH)_2$		0.44	0.68	1.10	1.29			301

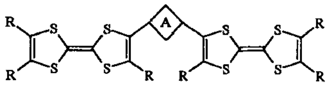
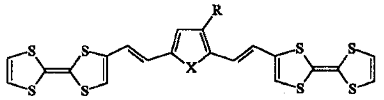
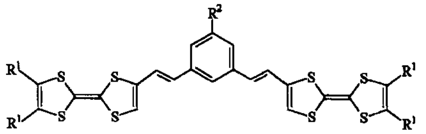
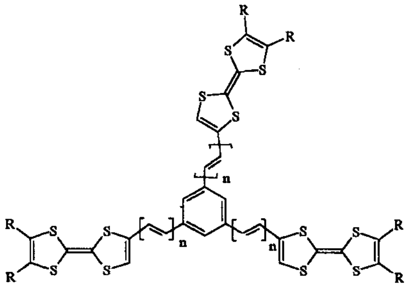
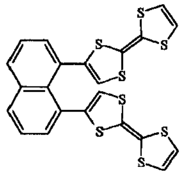
(*Table Continued*)

TABLE IV (*Continued*)

Compound	E_1^{Ox} [V]	E_2^{Ox} [V]	E_3^{Ox} [V]	E_4^{Ox} [V]	E_5^{Ox} [V]	E_6^{Ox} [V]	*References*
	0.54	0.69	1.06	1.22			301
							
R^1: SC_6H_{13} R^2: SC_5H_{11}-*i*	0.34	0.44	0.69	0.78	1.10	1.33[d]	846
R^1: SC_4H_9 R^2: OC_6H_{13}	0.34	0.45	0.78[a]		1.07	1.31[f]	846
R^1: SCH_2CH_2S R^2: OC_6H_{13}	0.28	0.42	0.68	(0.87)	1.08[f]		846
							
R^1: H R^2: OC_6H_{13}	0.31		0.61[g]	0.81	1.01	1.28[f]	299, 846
R^1: SC_2H_5 R^2: SC_5H_{11}-i	0.44	0.61	0.81	1.01	1.28[h]		846
							
R: C_6H_{13}	0.49	0.71	1.24	1.50			609
	0.40	0.56	0.93	0.97[a,j]			658
							
R^1: H R^2: H X: S Y: S	0.37	0.50	0.81	1.05[a]			847
R^1: $COOCH_3$ R^2: $COOCH_3$ X: S Y: S	0.56	0.70	1.07	1.30[a]			847
R^1: H R^2: H X: Se Y: S	0.42	0.54	0.81	(1.13)[a]			848
R^1: $COOCH_3$ R^2: $COOCH_3$ X: Se Y: S	0.59	0.73	1.09	(1.32)[a]			848
R^1: H R^2: H X: S Y: Se	0.39	0.52	0.87	(1.08)[a]			441
R^1: H R^2: H X: Se Y: Se	0.43	0.55	0.87	(1.11)[a]			441

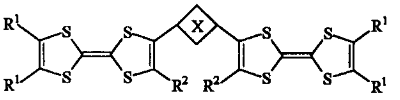
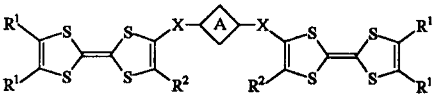
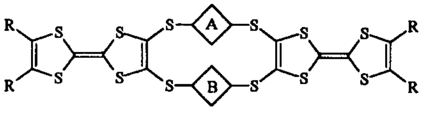
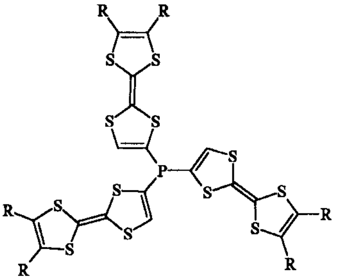
Parentheses indicate an irreversible redox reaction, [a]in benzonitrile, [b]0.05 MTBAT, *vs*. Ag/AgCl, in benzonitrile, [c]0.05 MTBAT, *vs*. Ag/AgCl, in dimethylformamide, [d]in 1,1,2-trichloroethane at 70°C, [e]two-electron transfer step, [f]in 1,1,2-trichloroethane, [g]poorly separated, [h]in 1,1,2-trichloroethane at 90°C, [i]in benzonitrile/carbon disulfide (1 : 1 v/v), [j]*vs*. Ag/AgCl, [k]in acetonitrile.

TABLE V Oxidation potentials of group 2 dimeric or trimeric tetrathiafulvalenes in benzonitrile (*vs.* Ag/AgCl electrode, 0.1 M Bu_4NClO_4)

Compound		E_1^{Ox} [V]	E_2^{Ox} [V]	*References*
				
R: H	A: 1,2-ethenediyl	0.41	0.71	662
R: H	A: 1,3-phenylene	0.40	0.81^a	645
R: H	A: 1,4-phenylene	0.35	0.82	644
R: H	A: 2,6-pyridinediyl	0.29	0.87^a	645
R: H	A: 2,5-thienediyl	0.38	0.81	644
R: H	A: $C{=}C(CH_3)_2$	0.39	0.72^a	650
R: H	A: $C{=}C(CH_2)_4$	0.39	0.73^a	650
R: H	A: C-9-fluoroenylidene	0.45	0.80^a	650
R: H	A: $C{=}C(C_6H_5)_2$	0.40	0.79^a	650
R: H	A: C-dithieno[2,3-b;2,3-d]-2,4-cyclopentadien-1-ylidene	0.48	0.82^a	650
R: SCH_3	A: C-9-fluorenylidene	0.56	0.77^a	650
R: SCH_3	A: $C{=}C(C_6H_5)_2$	0.53	0.79^a	650
				
R: H	X: S	0.39	0.67^b	719
R: CH_3	X: S	0.38	0.67^b	719
R: $(CH_2)_7CH_3$	X: S	0.37	0.66^b	719
R: H	X: Se	0.39	0.68^b	719
				
R^1: $SC_{12}H_{25}$	R^2: CH_2OH	0.50	0.91^{a,c}	849
R^1: $SC_{12}H_{25}$	R^2: CH_2OCO-1,4-phenylene-N-$CH_2(CH_2CH_2\text{-}O)_2\text{-}OCH_3$-3,4-fullero-2-pyrrolidinyl	0.51	0.92^{a,c}	849
				
R: H	n: O	0.29	0.77^a	645
R: SC_6H_{13}	n: 1, 2	0.48	0.85^{a,c}	723
R: $SC_{12}H_{25}$	n: 1, 2	0.48	0.85^{a,c}	723
		0.30	0.91^a	649

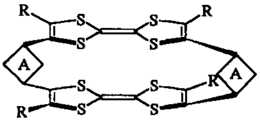
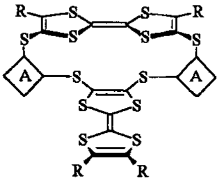
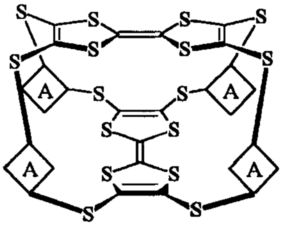
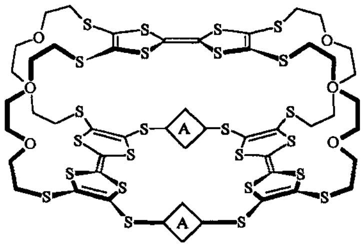
^{a}vs. sce, ^{b}in N,N-dimethylformamide, ^{c}in dichloromethane.

TABLE VI Oxidation potentials of group 3 dimeric or trimeric tetrathiafulvalenes in dichloromethane (*vs.* Ag/AgCl electrode, 0.1 M Et_4NPF_6 or 0.05 M, respectively, 0.1 M Bu_4NPF_6 or 0.1 M Bu_4NClO_4)

Compound				E_1^{Ox} [V]	E_2^{Ox} [V]	E_3^{Ox} [V]	E_4^{Ox} [V]	*References*
								
R^1: H	R^2: H	X: S		0.49	0.61	(0.86)		672
R^1: H	R^2: H	X: Se		0.49	0.61	(0.86)		672
R^1: H	R^2: H	X: Te		0.31	0.65	$(0.8)^{a}$		642
R^1: H	R^2: H	X: $Si(CH_3)_2$		0.29	0.38	0.77^{b}		639
R^1: CH_3	R^2: H	X: $Si(CH_3)_2$		0.22	0.32	0.82^{b}		639
R^1: CH_3	R^2:CH_3	X: $Si(CH_3)_2$		0.24	0.34	0.88^{b}		639
R^1: H	R^2: H	X: $P(C_6H_5)$		0.37	0.47	0.84^{b}		639
R^1: CH_3	R^2: H	X: $P(C_6H_5)$		0.28	0.38	0.88^{b}		639
R^1: CH_3	R^2: CH_3	X: $P(C_6H_5)$		0.23	0.36	0.76	0.87^{b}	639
								
R^1: CH_3	R^2: CH_3	A: CH_2	X: S	0.22	0.36	0.80^{b}		195
R^1: CH_3	R^2: CH_3	A: $(CH_2)_2$	X: S	0.23	0.36	0.74^{b}		195
R^1: CH_3	R^2: SCH_3	A: $(CH_2)_3$	X: S	0.39	0.43	0.84^{b}		850
R^1: CH_3	R^2:$COOCH_3$	A: $(CH_2)_3$	X: S	0.40	0.56	0.94^{c}		256
R^1: SCH_3	R^2: $S(CH_2)_2CN$	A: CH_2-5-*t*-C_4H_9-1, 3-phenylene-CH_2	X: S	0.55	0.63	0.91		794
R^1: $S(CH_2)_2S$	R^2: SCH_3	A: CH_2	X: S	0.47	0.55	(0.81)		851
R^1: $S(CH_2)_2S$	R^2: SCH_3	A: $(CH_2)_3$	X: S	0.48	0.56	0.88^{b}		850
R^1: $Se(CH_2)_2Se$	R^2: $SeCH_3$	A: $(CH_2)_3$	X: Se	0.48	0.57	0.89^{b}		850
R^1: $Se(CH_2)_2Se$	R^2: $Se(CH_2)_2CN$	A: $(CH_2)_3$	X: Se	0.51	0.57	0.88^{b}		850
								
R: SCH_3	A: S	B: S		0.57	0.68	1.15^{d}		852
R: SCH_3	A: CH_2-5-*t*-C_4H_9-1, 3-phenyleneCH_2	B: CH_2-5-*t*-C_4H_9-1, 3-phenyleneCH_2		0.44	0.63	0.90		794
R: SCH_3	A: CH_2-5-*t*-C_4H_9-1, 3-phenyleneCH_2	B: $CH_2CH_2OCH_2CH_2$		0.46	0.60	0.88		794
R: SCH_3	A: CH_2-5-*t*-C_4H_9-1, 3-phenyleneCH_2	B: $(CH_2CH_2O)_2CH_2CH_2$		0.55	0.63	0.91		794
								
R: H				0.35	0.47	0.54	0.86^{b}	343, 640
				0.47	$0.86^{b,c}$			640
R: CH_3				0.27	0.38	0.47	0.78^{b}	343

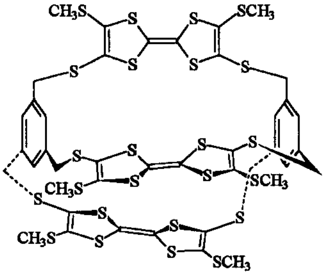
(*Table Continued*)

TABLE VI (*Continued*)

Compound			E_1^{Ox} [V]	E_2^{Ox} [V]	E_3^{Ox} [V]	E_4^{Ox} [V]	*References*
							
R: H	A: SCH_2S	X: S	0.35	0.48	(1.10)[d]		357
R: H	A: $S(CH_2)_2S$	X: S	0.41	0.56	0.83[d]		803
R: H	A: $S(CH_2)_3S$	X: S	0.40	0.50	0.78[d]		804
R: SCH_3	A: $CH_2C\equiv CCH_2$	X: S	0.43	0.64	0.91		354
R: $S[(CH_2)_2O]_2(CH_2)_2S$-1,3-dithiole-2-thione-4,5-diyl-$S(CH_2)_2[O(CH_2)_2]_2S$	A: $S(CH_2)_3S$	X: S	0.50	0.62	0.85		357
R: $S[(CH_2)_2O]_2(CH_2)_2S$-1,3-dithiole-2-thione-4,5-diyl-$S(CH_2)_2[O(CH_2)_2]_2S$	A: $S(CH_2)_2O(CH_2)_2S$	X: S	0.49	0.55	0.87		357
R: $COOCH_3$	A: $CH_2C\equiv CCH_2$	X: S	0.56	0.71	1.01	(1.24)	354
R: H	A: $S(CH_2)_2S$	X: Se	0.47	0.62	0.96[d]		807
R: H	A: $S(CH_2)_3S$	X: Se	0.51		0.93[d]		807
							
R: SCH_3	A: $(CH_2)_2$		0.56	0.66	0.77		359
R: SCH_3	A: $(CH_2)_3$		0.54	0.69	0.78		359
							
A: $(CH_2)_2$			(0.94)[d]				791, 810
A: $(CH_2)_3$			0.64	0.77	1.07	1.18[d]	810, 811
			0.57	0.70	0.98	1.11[d]	791, 792
A: $(CH_2)_4$			0.60		0.89[d]		791, 792
A: $(CH_2)_5$			0.46		0.74	0.85[d]	791, 792
A: $[(CH_2)_2O)_2](CH_2)_2$			0.52	0.65	0.85	0.91	778
							
A: $(CH_2)_3$			0.49	0.57	0.87		808

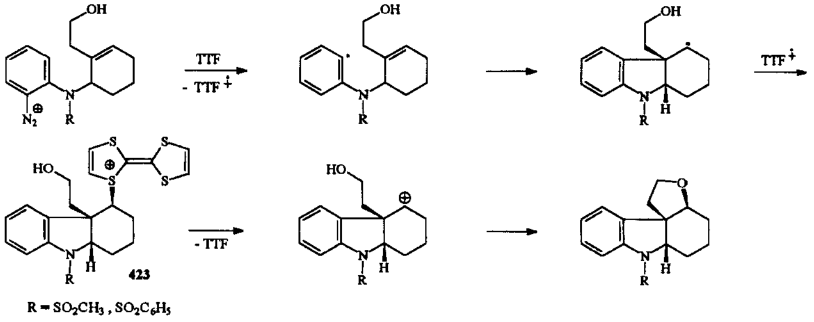
(*Table Continued*)

TABLE VI (*Continued*)

Compound	E_1^{Ox} [V]	E_2^{Ox} [V]	E_3^{Ox} [V]	E_4^{Ox} [V]	*References*
	0.405	0.50	0.59	0.87[e]	360, 361

Parentheses indicate an irreversible redox reaction, [a]in acetonitrile/tetrahydrofuran (5 : 1), [b]*vs.* sce, [c]in acetonitrile, [d]in benzonitrile, [e]in dichloromethane/acetonitrile (3 : 1).

the formation of an aryl radical. The formed aryl radical cyclizes to a new radical, which then couples with TTF radical cation to form a sulfonium salt **423**. In the final step, crossover to ionic chemistry is observed and TTF is regenerated by several nucleophiles via S_N1 mechanism. All reactions are stereocontrolled [855–858]. This chemistry has permitted the synthesis of complex molecules [855–866].



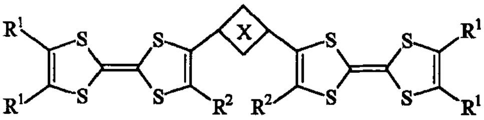
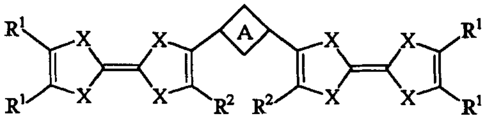
SCHEME 219

After removal of an electron from tetrachalcogenafulvalenes the radical cations or dications formed are stable and can be isolated as the corresponding salts in most cases. The formation constants *K* of the radical cations are calculable from the redox potentials [867].

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

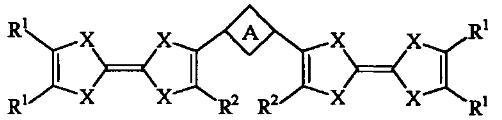
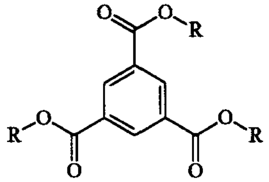
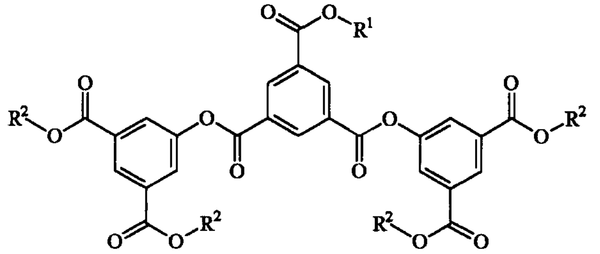
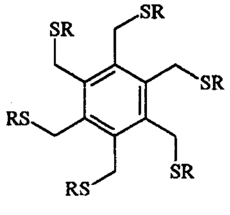
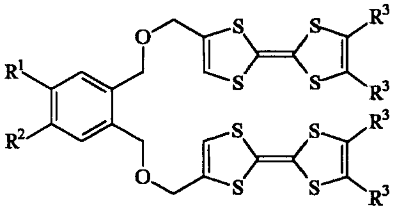
The radical cations give ESR spectra, the resolution of which depends on the solvent and the formation conditions. The line width increases from tetrathiafulvalene [189,832,868–873] to tetraselenafulvalene radical cations [874,875]. The low solubility of TTeF has so far thwarted the generation of radical cations and the recording of their ESR spectra [431]. The oxidation of TTF [876,877] and TSF [877,878] can take place electrochemically. With a low current single crystals are generated [878–880].

TABLE VII Oxidation potentials of group 4 dimeric or trimeric tetrathiafulvalenes in dichloromethane (*vs.* Ag/AgCl electrode, 0.1 M Bu_4NClO_4 or 0.05 M, respectively, 0.1 M Bu_4NPF_6)

Compound				E_1^{Ox} [V]	E_2^{Ox} [V]	*References*
						
R^1: H	R^2: H	X: Hg		0.35	$0.68^{a,b}$	453
R^1: CH_3	R^2: H	X: Hg		0.27	$0.66^{a,b}$	453
R^1: CH_3	R^2: CH_3	X: Hg		0.28	$0.63^{a,b}$	453
R^1:$S(CH_2)_2S$	R^2: H	X: $(CH_2)_2$		0.45	0.85^{b}	853
						
R^1: H	R^2: H	A: $S(CH_2)_3S$	X: S	0.44	0.78	487
R^1: H	R^2: H	A: $S(CH_2)_4S$	X: S	0.44	0.81	487
R^1:H; $C_{17}H_{35}$	R^2: H	A: $S(CH_2)_4S$	X: S	0.49	0.84^{c}	259
R^1: CH_3	R^2: H	A: $S(CH_2)_2S$	X: S	0.53	0.87^{c}	607
R^1: CH_3	R^2: H	A: $S(CH_2)_3S$	X: S	0.46	0.78^{c}	607
R^1: CH_3	R^2: H	A: $S(CH_2)_4)S$	X: S	0.44	0.78^{c}	607
R^1: CH_3	R^2: CH_3	A: $S(CH_2)_3S$	X: S	0.28	0.75^{b}	151
R^1: CH_3	R^2: CH_3	A: $S(CH_2)_{10}S$	X: S	0.27	0.77^{b}	151
R^1: CH_3	R^2: CH_3	A: $SCH_2C_6H_4CH_2S$ (1,2)	X: S	0.29	0.79^{b}	151
R^1: CH_3	R^2: CH_3	A: $SCH_2C_6H_4CH_2S$ (1,3)	X: S	0.26	0.75^{b}	151
R^1: CH_3	R^2: CH_3	A: $SCH_2C_6H_4CH_2S$ (1,4)	X: S	0.28	0.76^{b}	151
R^1: H; $C_{17}H_{35}$	R^2: $COOCH_3$	A: $S(CH_2)_3S$	X: S	0.59	0.93^{c}	259
R^1: H; $C_{17}H_{35}$	R^2: $COOCH_3$	A: $S(CH_2)_4S$	X: S	0.59	0.88^{c}	259
R^1: CH_3	R^2: $COOCH_3$	A: $S(CH_2)_2S$	X: S	0.60	0.94^{c}	607
R^1: CH_3	R^2: $COOCH_3$	A: $S(CH_2)_4S$	X: S	0.56	0.91^{c}	607
R^1: SCH $(C_{17}H_{35})CH_2S$	R^2: $COOCH_3$	A: $S(CH_2)_3S$	X: S	0.64	1.03^{d}	259
R^1: H	R^2: $SCH{=}CH_2$	A: $S(CH_2)_3S$	X: S	0.48	$0.79^{b,d}$	679
R^1: H	R^2: $SCH{=}CH_2$	A: $S(CH_2)_4S$	X: S	0.48	$0.80^{b,d}$	679
R^1: H	R^2: $SCH{=}CH_2$	A: $S(CH_2)_5S$	X: S	0.48	$0.81^{b,d}$	679
R^1: CH_3	R^2: $S(CH_2)_2CN$	A: $S(CH_2)_3S$	X: S	0.45	0.87^{b}	850
R^1: SCH_3	R^2: $S(CH_2)_2CN$	A: $S(CH_2)_3S$	X: S	0.57	0.90	822
R^1: $S(CH_2)_2S$	R^2: $S(CH_2)_2CN$	A: $S(CH_2)_3S$	X: S	0.56	0.89^{b}	850
R^1: SCH_3	R^2: $S(CH_2)_2CN$	A: $SCH_2C{\equiv}CCH_2S$	X: S	0.58	0.88	354
R^1: SCH_3	R^2: $S(CH_2)_2CN$	A: $SCH_2C{\equiv}C{-}C{\equiv}CCH_2S$	X: S	0.57	0.87	354
R^1: H	R^2: H	A: $SCH_2C_6H_4CH_2S$ (1,3)	X: S	0.45	0.79	676
R^1: H	R^2: H	A: SCH_2(5-CH_2S-tetrathiafulvalen-4-yl) $C_6H_3CH_2S$ (1,3)	X: S	0.47	0.81	676
R^1: SCH_3	R^2: $S(CH_2)_2CN$	A: $SCH_2C_6H_4CH_2S$ (1,4)	X: S	0.60	0.93	354
R^1: SCH_3	R^2: $S(CH_2)_2CN$	A: $SCH_2C_6H_4C_6H_4CH_2S$ (1, 4)	X: S	0.60	0.93	354
R^1: H	R^2: H	A: $S(CH_2)_2OCOO(CH_2)_2S$	X: S	0.46	0.81	676
R^1: H	R^2: H	A: $S(CH_2)_2$ $OCOCH_2COO(CH_2)_2S$	X: S	0.47	0.78	676
R^1: H	R^2: H	A: $S(CH_2)_2OCOCH(C_{18}H_{37})$ $COO(CH_2)_2S$	X: S	0.47	0.79	676
R^1: H	R^2: H	A: $S(CH_2)_2OCO2,3\text{-}(CH_3)_2$-1,4-dithiafulvene-6, 6-diyl-$COO(CH_2)_2S$	X: S	0.44	0.88	676
R^1: H	R^2: H	A: $S(CH_2)_2OCO$-1,1′-ferrocenediyl-$COO(CH_2)_2S$	X: S	0.37	0.71^{c}	678

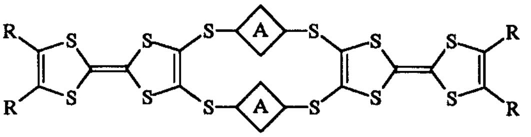
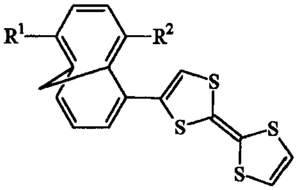
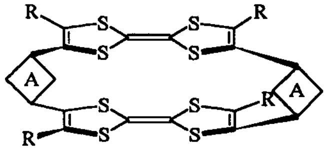
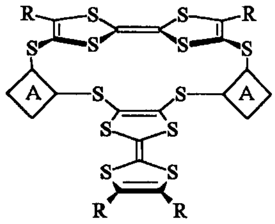
(*Table Continued*)

TABLE VII (*Continued*)

Compound				E_1^{Ox} [V]	E_2^{Ox}	*References*
R^1: SCH_3	R^2: SCH_3	A: S–S	X: S	0.61	0.93[b]	685
R^1: H	R^2: H	A: $(CH_2)_2$	X: Se	0.46	0.91[d]	418
R^1: H	R^2: H	A: $(CH_2)_3$	X: Se	0.45	0.96[d]	418
R^1: H	R^2: H	A: $(CH_2)_4$	X: Se	0.48	0.90[d]	418
R^1: H	R^2: H	A: $S(CH_2)_2S$	X: Se	0.56	1.00[d]	418
R^1: H	R^2: H	A: $S(CH_2)_3S$	X: Se	0.54	0.98[d]	418
						
R: $S(CH_2)_2S$	A: OCO-1, 4-phenyleneCOO			0.49	0.90[b]	570
						
R: $(CH_2)_2STTF$				0.45	0.78	676
R: CH_2TTF				0.42	0.84[c]	575
						
R^1: $C_6H_3(COOCH_2TTF)$-3,5	R^2: CH_2TTF			0.45	0.86[j]	676
						
R: 5,4′,5′-$(SCH_3)_3$-tetrathiafulvalen-4-yl				0.55	0.88	580
						

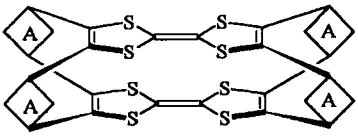
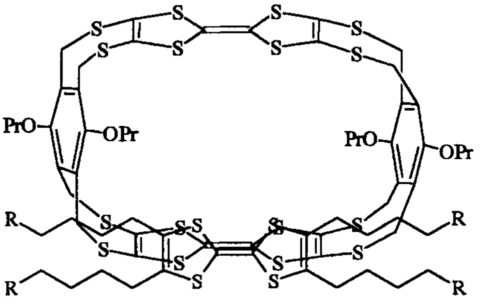
(*Table Continued*)

TABLE VII (*Continued*)

Compound			E_1^{Ox} [V]	E_2^{Ox}	*References*
R^1: CN	R^2: CN	R^3: H	0.51	$0.77^{\mathrm{a,I}}$	613
R^1: CN	R^2: CN	R^3: $\mathrm{SC_6H_{13}}$	0.56	0.92^{d}	614
R^1: CN	R^2: Br	R^3: $\mathrm{SC_6H_{13}}$	0.55	0.92^{d}	614
R^1: Br	R^2: Br	R^3: $\mathrm{SC_6H_{13}}$	0.54	0.92^{d}	614
					
R: $\mathrm{S(CH_2)_2S}$	A: $\mathrm{(CH_2)_2}$		0.59	$(0.84)^{\mathrm{c}}$	795
R: $\mathrm{SCH_3}$	A: $\mathrm{CH_2C_6H_4CH_2}$ (1,4)		0.57	0.93	354
R: $\mathrm{SC_5H_{11}}$	A: $\mathrm{CH_2C_6H_4CH_2}$ (1,4)		0.57	0.90	354
R: $\mathrm{SC_5H_{11}}$	A: $\mathrm{CH_2C_6H_4CH_2}$ (1,4)		0.57	0.90	354
R: $\mathrm{SCH_3}$	A: $\mathrm{CH_2C_6H_4C_6H_4CH_2}$ (1,4)		0.58	0.93	354
R: $\mathrm{SC_5H_{11}}$	A: $\mathrm{CH_2C_6H_4C_6H_4CH_2}$ (1,4)		0.57	0.92	354
					
R^1: tetrathiafulvalen-4-yl	R^2: H		0.40	$0.79^{\mathrm{b,d}}$	649
R^1: H	R^2: tetrathiafulvalen-4-yl		0.29	$0.89^{\mathrm{b,d}}$	649
					
R: $\mathrm{CH(OC_2H_5)_2}$	A: $\mathrm{CHNN(CH_3)PO}$ $\mathrm{(C_6H_5)N(CH_3)NCH}$		0.61	$1.05^{\mathrm{b,f}}$	728
R: H	A: $\mathrm{S(CH_2)_4S}$		0.45	0.83^{d}	358
R: $\mathrm{CH_3}$	A: $\mathrm{S(CH_2)_4S}$		0.48	0.87^{b}	805
R: $\mathrm{C_6H_4Cl}$-4	A: $\mathrm{S(CH_2)_3S}$		0.18	0.45	347
R: $\mathrm{SCH_3}$	A: $\mathrm{SCH_2C{\equiv}C{-}C{\equiv}CCH_2S}$		0.55	0.83	354
R: $\mathrm{SCH_3}$	A: $\mathrm{SCH_2C_6H_4C_6H_4CH_2S}$ (1,4)		0.58	0.85	354
R: $\mathrm{SCH_3}$	A: $\mathrm{SCH_2C_6H_4CH_2C_6H_4CH_2S}$ (1,4)		0.49	0.87	348
R: $\mathrm{SCH_3}$	A: $\mathrm{S[(CH_2)_2O]_2(CH_2)_2S}$		0.55	0.92	365
					
R: $\mathrm{SCH_3}$	A: $\mathrm{(CH_2)_2O(CH_2)_2}$		0.46	0.72	359
R: $\mathrm{SCH_3}$	A: $\mathrm{[(CH_2)_2O]_2(CH_2)_2}$		0.55	0.91	365
R: $\mathrm{SCH_3}$	A: $\mathrm{CH_2C_6H_4CH_2}$ (1,4)		0.50	0.77	359

(*Table Continued*)

TABLE VII (*Continued*)

Compound	E_1^{Ox} [V]	E_2^{Ox} [V]	*References*
			
A: $SCH_2C(CH_3)_2CH_2S$	0.68	1.00[k]	809
A: $S(CH_2)_2O(CH_2)_2S$	0.53	1.00	794
A: $S(CH_2)_2O[2,6\text{-}(CH_3)_2\text{-}1,$ 4-phenylene]-1, 1-cyclohexanediyl-$[3,5\text{-}(CH_3)_2\text{-}1,4\text{-phenylene}]O(CH_2)_2S$	0.58	0.91	751
	0.36 1.01	1.06[b,a]	854
R: $5,4',5'\text{-}(SCH_3)_3$-tetrathiafulvalen-4-yl	0.52	0.82[g,h]	333

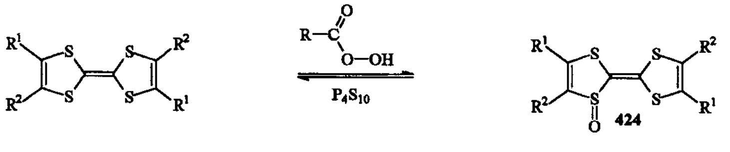
Parentheses indicate an irreversible redox reaction, [a]in *N*,*N*-dimethylformamide, [b]*vs.* sce, [c]in acetonitrile, [d]in benzonitrile, [e]the small potential difference reflects a small Coulomb interaction, [f]in 1,1,2-trichloroethane, [g]in dichloromethane/acetonitrile (3 : 1), [h]broadened first wave indicates a non-simultaneous loss of electrons from the central and peripheral TTF, [i]0.1 M TEAHP, [j]in dichloromethane/acetonitrile (1 : 1), [k]in benzonitrile/carbon disulphide (1 : 1), [l]unstrained TTF, [m]strained TTF.

Also the application of oxidation agents affords radical cations or dications. TTF can be oxidized, e.g. with halogens [189,868,881,882], thiocyanogen [883], metal salts [884–886], hydrogen peroxide [887,888], aryldiazonium salts [889,890], lead(IV) acetate [189], lead(IV) oxide [836,891], oxoaminium salts [892], or halocarbons in the presence of light [893,894], and TSF, for example, with iodine [390,895] or lead(IV) oxide [405].

Radical cations are also formed in comproportionation reactions between the dications and the parent tetrathia- or tetraselenafulvalenes, respectively [405,836,891].

Radical cation salts of TTF are able to initiate the cationic polymerization of electron-rich vinyl monomers (vinyl ethers, 4-methoxystyrene, *N*-vinyl carbazole) [896].

Reduction of the monocations and dications with sodium bisulfite regenerates the corresponding TTF or TSF [390,868]. When TTF are oxidized with 3-chloroperbenzoic acid the corresponding tetrathiafulvalene *S*-oxides are formed [897,898]. The tetrathiafulvalene *S*-oxides **424** are also formed under the influence of oxygen on TTF [898]. Therefore TTF should be synthesized under exclusion of oxygen. With phosphorus pentasulfide the tetrathiafulvalene *S*-oxides **424** can be converted back to the corresponding TTF [897].



SCHEME 220

7.2.2. *Spectroscopic Behaviour*

The TTF, TSF, and TTeF have several bands in the UV–Vis 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 ringsize in cycloalkyl substituted TTF the longest-wavelength visible absorption is clearly shifted bathochromically, it is only slightly influenced by 1,4-substituents in the aryl group [836]. 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 [221,899–901]. From a comparison of quantum-chemical calculations with experimental absorption spectra an assignment as an $n \rightarrow \pi^*$ transition [901] and a $\pi \rightarrow \sigma^*$ transition [832] is also possible.

As a rule the radical cations 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 an absorption at shorter wavelength than the corresponding TTF. In the series of the tetrathiafulvalene radical cations 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 (Fig. 5) [836].

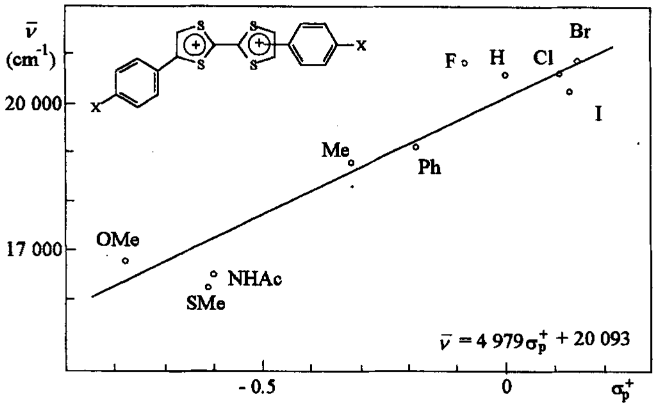
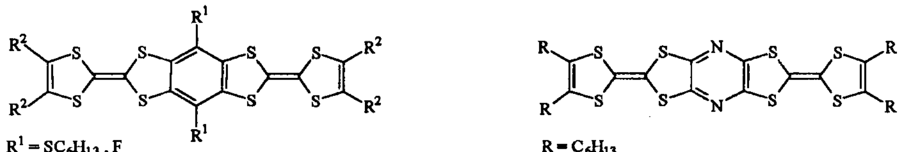


FIGURE 5 Wavenumbers of the longest-wavelength band of 2,6(7)-diaryl substituted TTF dications as a function of substituent constants.

Radical cations of type **425** and **426** show an intense and broad absorption band in the near-IR region (1600–1700 and 2500 nm, respectively). These low-energy absorption bands are assigned to intervalence transitions, caused by unequally distributed charge between the two chromophores. Theoretical calculations also point out mixed valence charge transfer involving these localized cation radical moieties, as usual electronic transitions, from the ground state to at least one nonadiabatically coupled low-lying excited state [609].



$R^1 = SC_6H_{13}$, F
$R^2 = C_6H_{13}$
425

$R = C_6H_{13}$
426

SCHEME 221

Vinylogous TTF with great extension of the conjugation between the two 1,3-dithiole moieties show also low-energy absorption bands till in the near IR region (900–1500 nm) [478].

^{77}Se NMR spectroscopy shows the formation of a mixture of *cis/trans* isomers in the synthesis of asymmetrically 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 [902,903].

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 (SCR) radical [904]. The main fragmentation of tetrathiafulvalene-fused thiophenes is the fragmentation of one of the 1,3-dithiole rings with subsequent loss of CS [905]. Fragmentation of substituted TTF depends on the type of substituent [152,906–910].

7.3. Charge Transfer Complexing of Tetrathia-, Tetraselena-, and Tetratellurafulvalenes

7.3.1. Optical Properties of Charge Transfer Complexes

In non-polar solvents TTF or derivatives form with electron acceptors, like quinones [911], carbon tetrachloride [833,893] or TCNQ [912], charge transfer complexes. In their spectra they show a new absorption band which can 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 value of the solvent (Fig. 6) and decreasing oxidation potential of the TTF (Fig. 7) [912].

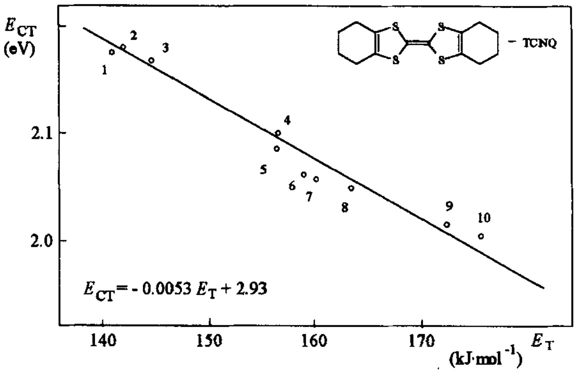


FIGURE 6 Solvent dependence of the charge transfer absorption of the octamethylenetetrathiafulvalene–TCNQ charge transfer complex (1 *t*-butylbenzene, 2 toluene, 3 benzene, 4 chlorobenzene, 5 bromobenzene, 6 iodobenzene, 7 1,2-dicholorbenzene, 8 chloroform, 9 dichloromethane, 10 1,2-dichloroethane).

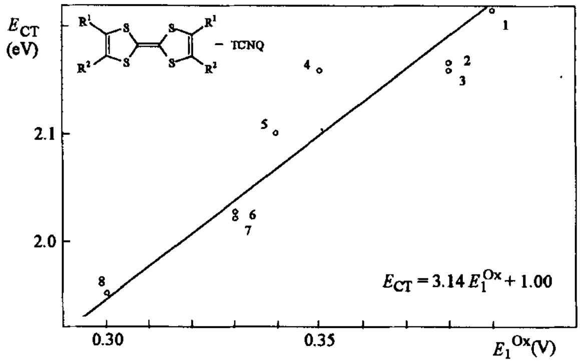


FIGURE 7 Charge transfer absorption of substituted TTF–TCNQ charge transfer complexes in chloroform as a function of half-wave oxidation potentials.

In acetone a complexation between TTF derivatives and the tetracationic *para–para* cyclophane π-acceptor cyclobis-(paraquat-1,4-phenylene) is observed, where the TTF core is located within the cyclophane. The association constants K_a increase with increasing donor properties and extension of the π-system of the TTF derivative. The following relationship is obeyed:

$$-\Delta G^\circ = k_1 + T\Delta S^\circ + \frac{k_2\beta^2}{E_1^{\mathrm{Ox}} - E_1^{\mathrm{Red}}}$$

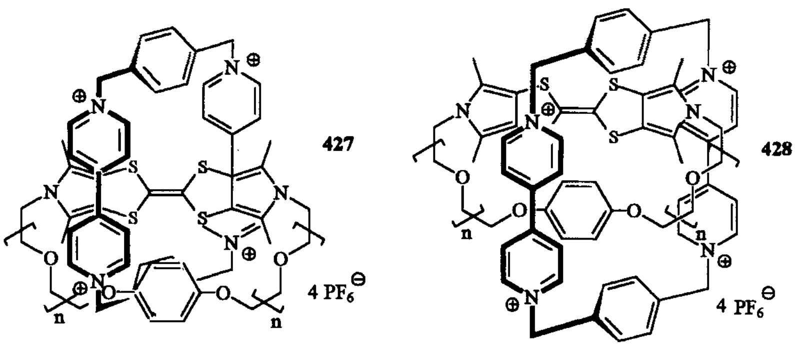
k_1, k_2 = constants, β = overlap integral between D and A, E_1^{Ox}, E_1^{Red} = first redox potential of D and A.

^{1}H NMR measurements show that the kinetics for complexation–decomplexation of the TTF derivatives with the cyclophane is related to the bulkiness of the TTF derivative [913]. A CT absorption between 800 and 900 nm is observed [913,914]. *Meta–para* cyclophanes form weaker CT complexes with TTF derivatives than the corresponding *para–para* cyclophanes [915]. Analogous results are received in the complexation of other TTF or TSF derivatives with cyclobis(paraquat-1,4-phenylene) [916].

Electrochemical oxidation of the TTF to the radical cation leads to a decomplexation, which is visible by a colour change of the solution from dark green to pale brown. This process is reversible and opens the possibility for an application as electrochemical controlled molecular switch [917].

In the three-component system TTF, cyclobis(paraquat-1,4-phenylene), and 1,5-dinaphtho[38]crown-10 different complexation states can be adjusted in dependence from the oxidation state of TTF. The mixture behaves as a three-pole system since TTF can be (1) uncomplexed (in the $TTF^{\bullet +}$ state), (2) complexed with cyclobis(paraquat-1,4-phenylene) (in the TTF state), or (3) complexed with 1,5-dinaphtho[38]crown-10 (in the TTF^{2+} state). The complexations/decomplexations are occurring rapidly compared to the time scale of the electrochemical experiments [918].

In catenanes with the two donor units, TTF moiety and 1,4-dioxybenzene moiety, the complexation with cyclobis(paraquat-1,4-phenylene) leads to a complexation as well the TTF moiety **427** as the 1,4-dioxybenzene moiety **428** and as a result two charge transfer absorption bands ($n = 1$, $\lambda_{max} = 699$ nm, only CT interaction with TTF; $n = 2$, 3, $\lambda_{max} = 410$ nm, CT interaction with 1,4-dioxybenzene; $\lambda_{max} = 920$ nm, CT interaction with TTF) are observed [782].

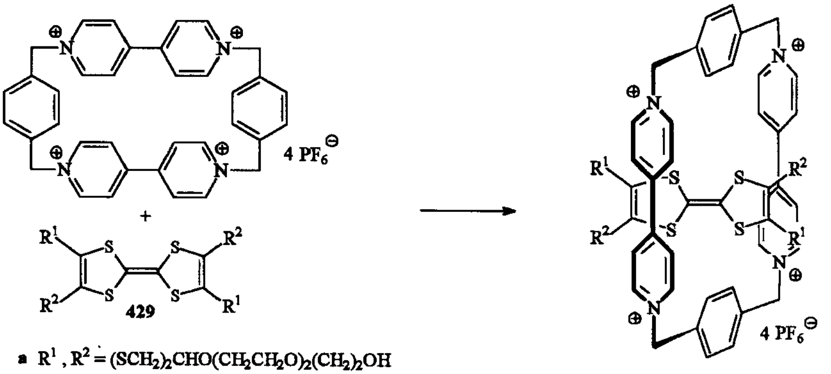


427

428

SCHEME 222

Wirelike TTF derivatives **429** form with cyclobis(paraquat-1,4-phenylene) pseudorotaxanes or rotaxanes with CT absorptions (**a**: $\lambda_{max}^{MeCN} = 768$ nm [825], **b**: $\lambda_{max}^{MeCN} =$ 830 nm [831], **c**: $\lambda_{max}^{MeCN} = 850$ nm [826], **d**: $\lambda_{max}^{DMSO} = 752$ nm [827]). Also a pyrrolo [3,4-*d*] and a bis(pyrrolo[3,4-*d*]) afford with cyclobis(paraquat-1,4-phenylene) rotaxanes, which show CT absorptions ($\lambda_{max}^{acetone} = 810$ nm [830], $\lambda_{max}^{MeCN} = 807$ nm [829], respectively). The complexation and formation of pseudorotaxanes mostly occurs rapidly however, in the case of **429c** the threading process is much slower because of the steric hindrance of the terminal 4-*t*-butyl groups [826].

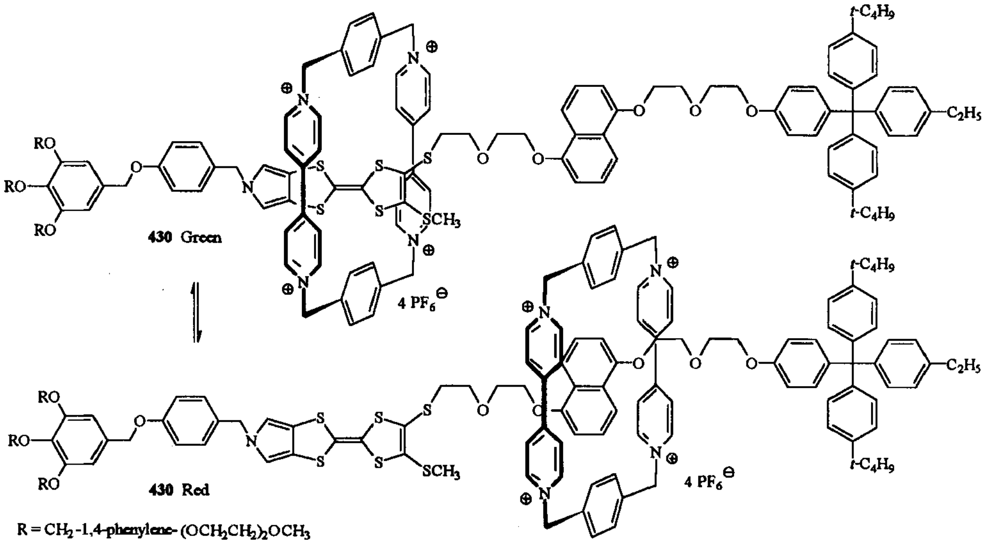


a R^1, R^2 = $(SCH_2)_2CHO(CH_2CH_2O)_2(CH_2)_2OH$
b R^1 = H, R^2 = $CH_2O(CH_2CH_2O)_3(CH_2)_2OH$
c R^1 = H, R^2 = $CH_2O(CH_2CH_2O)_3(CH_2)_2O$-1,4-phenylene-$C(CH_3)_3$
d R^1, R^2 = $(SCH_2)_2CHO(CH_2CH_2O)_3(CH_2)_2O$-1,4-phenylene-$O(CH_2CH_2)_2(CH_2)_2O$-1,4-phenylene-$C(C_6H_5)_3$

SCHEME 223

Two linearly linked TTF dimer and TTF trimer form rotaxanes with cyclobis(paraquat-1,4-phenylene) which reveal CT absorptions in acetonitrile ($\lambda_{max} = 748$ and 788 nm, respectively) [829].

In the rotaxane **430** with the TTF and the 1,5-dioxynaphthalene unit as donor a 1 : 1 mixture of two stable translational isomers are present. **430** Green is characterized as being the TTF unit located inside the cyclophane and **430** Red the 1,5-dioxynaphthalene unit located inside the cyclophane, indicated by different CT absorptions in acetone (**430** Green, $\lambda_{max} = 805$ nm; **430** Red, $\lambda_{max} = 540$ nm) [919].



R = CH_2-1,4-phenylene-$(OCH_2CH_2)_2OCH_3$

SCHEME 224

Cyclic TTF derivatives provide with cyclobis(paraquat-1,4-phenylene) catenanes, which display CT absorptions in the visible or NIR region [365,783].

In the case of the weak acceptor C_{60} the new absorption band is only observed in the solid state (X-ray photoelectron or IR spectroscopy) [920–926].

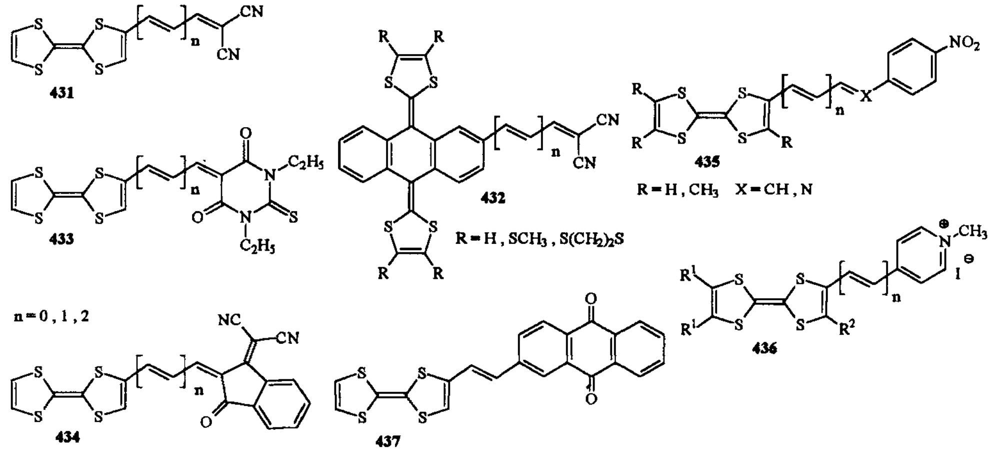
Dicyanovinylene–TTF derivatives **431**, in which both donor and acceptor moieties are separated by one or two ethylenic bonds, are CT complexes of the D–A type with conjugation between D and A and show a broad intramolecular charge transfer absorption around 600 nm with solvatochromic properties ($n = 1, \lambda_{max}^{MeCN} = 596$ nm, $\lambda_{max}^{DCM} = 618$ nm) and a rather unusual hypsochromic shift when the extended system is increased ($n = 0$, $\lambda_{max} = 624$ nm; $n = 1$, $\lambda_{max} = 618$ nm; $n = 2$, $\lambda_{max} = 608$ nm; in dichloromethane) [699,700]. Analogous properties exhibit dicyanovinylene derivatives of quinoid TTF **432** [704] (For a review of covalently linked TTF derivatives to an electron acceptor see [58].)

The same hypsochromic shift of the charge transfer absorption is observed on increasing number of double bonds in compounds **433** [703] ($n = 0$, $\lambda_{max} =$ 716 nm; $n = 1$, $\lambda_{max} = 661$ nm; $n = 2$, $\lambda_{max} = 646$ nm; in DMSO) or compounds **434** [702] ($n = 0$, $\lambda_{max} = 798$ nm; $n = 1$, $\lambda_{max} = 726$ nm; $n = 2$, $\lambda_{max} = 690$ nm; in dichloromethane).

TTF derivatives **435** connected by ethylenic bridges to the 4-nitrophenyl unit as acceptor display in dichloromethane a broad CT absorption around 500 nm with small influence of substituents and extension of the π-system [705].

Also in the *N*-methylpyridinium-substituted TTF **436** ($R^1 = R^2 = CH_3$, $n = 0$) [648], ($R^1 = SCH_3$, $R^2 = H$, $n = 0$) [927] and in the vinylogue derivative ($R^1 = R^2 = H$, $n = 1$) [690] a broad intramolecular CT absorption in DMSO ($\lambda_{max} = 561$, 540 and 552 nm, respectively) with a negative solvatochromism is observed.

The TTF derivative **437** with the conjugatively connected acceptor 9,10-anthraquinone shows an intramolecular CT absorption in dichloromethane ($\lambda_{max} = 530$ nm) [541].



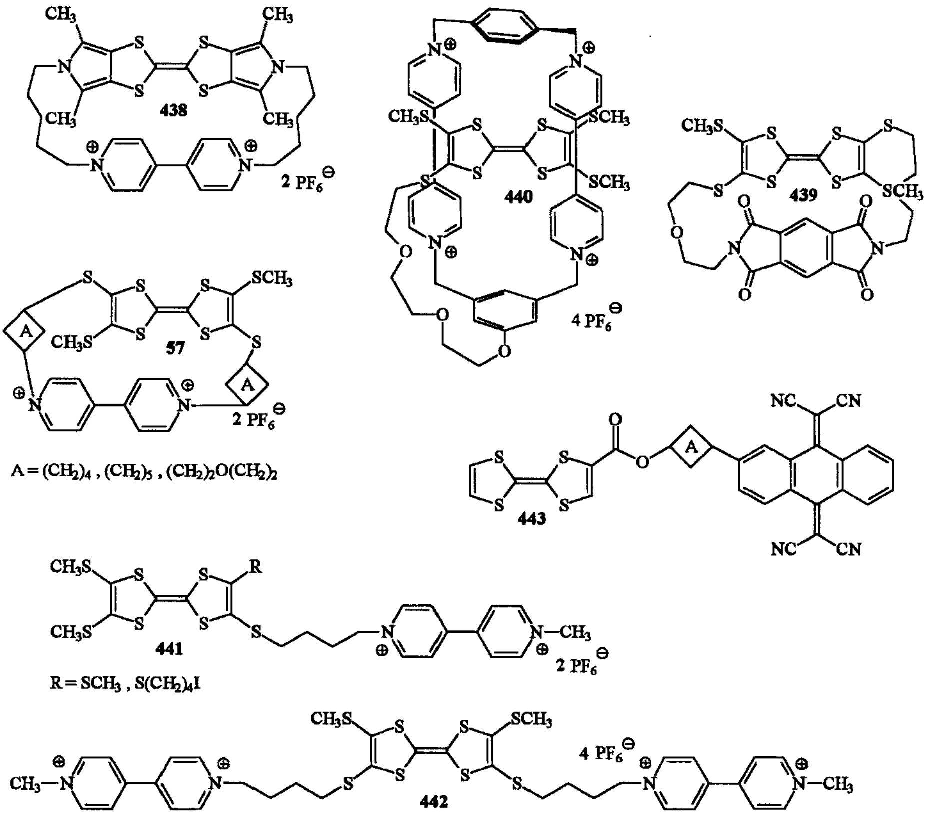
SCHEME 225

In the D–A type CT complexes **438**, **57** and **439** donor and acceptor moieties are connected by two bridges and held rigidly in close proximity, resulting CT absorptions in acetonitrile (**438**: $\lambda_{max} = 640$ nm, **57**: [$R = (CH_2)_4$] $\lambda_{max} = 673$ nm) [349] or in dichloromethane (**439**: $\lambda_{max} = 590$ nm) [356].

In the TTF derivative **440** the linker between donor and acceptor is long enough for an anchimeric CT complexation and the equilibrium between complexed **440** and decomplexed form is established. After 20 h a constant CT absorption (λ_{max}^{MeCN} = 785 nm) of the anchimeric complex **440** is observed [915,928].

In the same way a CT complexation in dichloromethane is observed in a TTF dimer of the double linkage type **370** with a tethered pyromellitic diimide acceptor [915].

Also in the TTF derivatives **441** and **442** donor and acceptor are connected by one chain, thus allowing the system to adopt an open conformation with no intramolecularly interaction in the solid state. But in acetonitrile solution intramolecular CT is observed. The possibility that intermolecular CT interaction may play a part in these systems are discounted by examination of solutions of tetramethylthio-TTF and the PF_6^- salt of the bipyridinium cation, no CT absorptions are found [349]. Despite a non-conjugative connecting between the donor and acceptor in **443** a very weak broad CT absorption ($A = CH_2$, λ_{max}^{MeCN} = 420–680 nm [929]; in dichloromethane, $A = CH_2CH_2N(CH_3)SO_2$, λ_{max} = 430 nm, A = 1,4-phenylene–OSO_2, λ_{max} = 445 nm [563]) is observed, assigned to an intramolecular charge transfer.



SCHEME 226

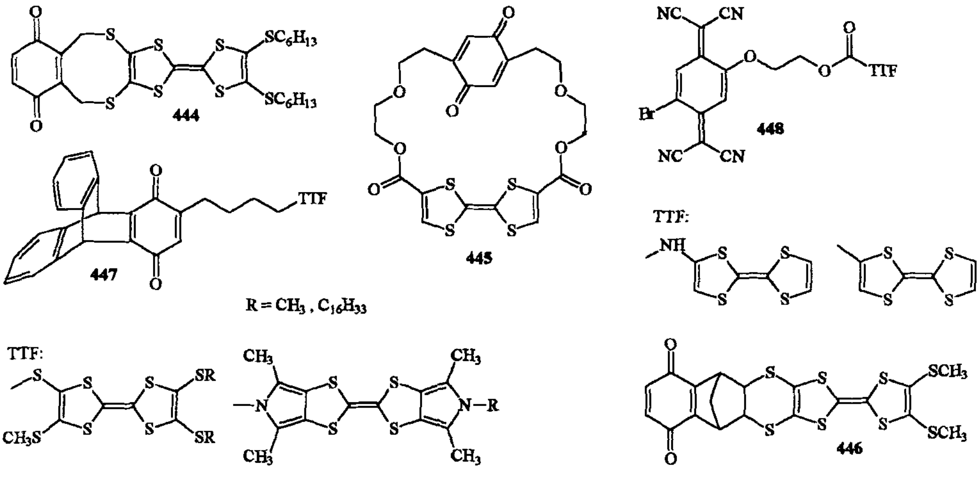
In D–A type CT complexes linking covalently TTF derivatives to C_{60} no CT absorption is observed [707–710,713], but if D and A are linked by flexible σ-chains the UV–Vis spectra show a new, broad, weak shoulder extending from 400 to 1000 nm, which may be an intervalence transfer band centred at about 800 nm ($\varepsilon \sim 200$). Photolysis of these molecules in a frozen toluene solution produced radicals by electron transfer [711].

In the CT system **444** and **445** donor and acceptor are nonconjugatively connected and only a through space interaction is possible, no charge transfer band is observed [761]. The quinone and TTF in **445** do not lie directly above and below each other, no CT interaction is possible [784].

In **446** D and A are also linked by nonconjugated rigid cyclic rings, but the molecule shows a bent structure in which the plane of D lies above the plane of A. Therefore, in solution a broad absorption band in the 500 to 950 nm region, centered at *ca.* 685 nm ($\varepsilon \sim 310$), is observed and assigned to an intramolecular CT interaction [930].

In the D–A compounds **447** [931,932] and **448** [555] donor and acceptor moieties are connected by one chain which does not permit a close proximity of the TTF and quinone moieties. Therefore, also in these compounds no CT absorptions are observed.

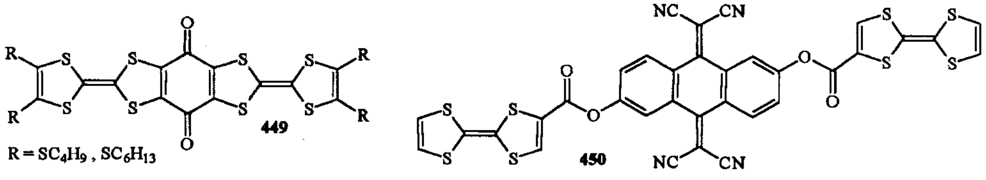
In a polyester dendrimer containing both TTF (4,8) and anthraquinone units (2,4) around a benzene-1,3,5-triester core, only in the higher generation molecule (8 TTF and 4 AQ units) is a very weak ($\varepsilon < 250$) broad absorption band in the 460–750 nm region in acetonitrile observed, arising from intramolecular CT from TTF to anthraquinone units [577].



SCHEME 227

In CT complexes of D–A–D type **449**, where the donor and acceptor units are annelated with strong conjugative interaction, a very broad low-energy band is observed, resulting from intramolecular charge transfer from donor to acceptor moiety. This absorption shows a solvatochromic effect in solvents of different polarity up to 90 nm (R = *n*-Hex, $\lambda_{max}^{dioxane} = 787$ nm, $\lambda_{max}^{toluene} = 819$ nm, $\lambda_{max}^{DCM} = 877$ nm) and a further bathochromic shift in the solid state ($\lambda_{max} = 1042$ nm) [345].

Although in the D–A–D compound **450** donor and acceptor are connected by σ-bridges a small CT interaction takes place in acetonitrile, indicated by a very weak broad CT absorption in the $\lambda = 420$–680 nm region [929].

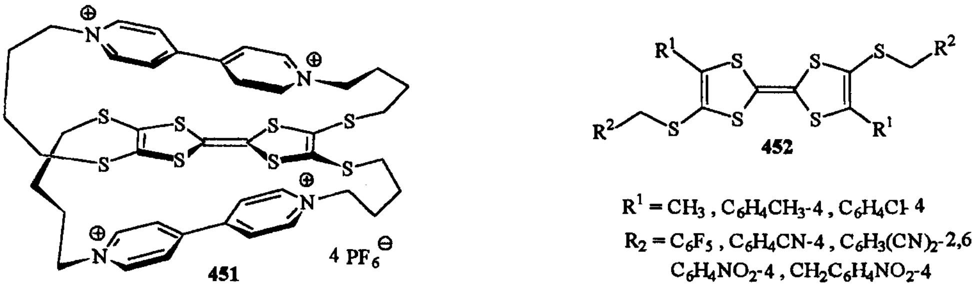


449 $R = SC_4H_9, SC_6H_{13}$

450

SCHEME 228

The A–D–A system **451** in which the donor TTF is sandwiched between two bipyridinium acceptor moieties shows a CT interaction, evidenced by a broad CT absorption ($\lambda_{max}^{MeCN} = 645\,nm$) [793]. The A–D–A triads **452** in which the two acceptor units (R^2 = electron deficient benzene derivatives) are covalently bonded (without conjugation between donor and acceptor) to a TTF moiety display no intramolecular CT interaction [316].



451 $4\ PF_6^{\ominus}$

452

$R^1 = CH_3, C_6H_4CH_3\text{-}4, C_6H_4Cl\text{-}4$

$R_2 = C_6F_5, C_6H_4CN\text{-}4, C_6H_3(CN)_2\text{-}2,6, C_6H_4NO_2\text{-}4, CH_2C_6H_4NO_2\text{-}4$

SCHEME 229

7.3.2. Electrical Properties of Charge Transfer Complexes

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 crystals of the charge transfer complex tetrathiafulvalene–TCNQ show metallic conductivity [933]. 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 0.5–0.9 electrons 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 neighbouring 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 [934].

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 [935].

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 [936].

- 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 incompletely 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^-, ClO_4^-, ReO_4^-, PF_6^-, $SbCl_6^-$, AsF_6^-) 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 behaviour.

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 interaction 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 transition is partially or completely suppressed.

The formation of segregated and uniform stacks with partial charge transfer essentially depends on steric and electronic properties of both complexing agents and crystallization conditions. The investigation of these problems has been the subject of many conferences and reviews, some of which are referred to here [1–80].

A small selection of charge transfer complexes with high conductivity and semiconducting properties is shown in Table VIII.

Doping of an electrically insulating polymer (polyester, polycarbonate, polysulfone, polyacrylate, polyacetal) 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.%. This can be explained by the fact that the conductive charge transfer complex is not statistically dispersed in

TABLE VIII Electric conductivity, temperature of metal–insulator transition and structure of selected charge–transfer complexes

Complex	σ_{RT} [S-cm^{-1}]	T_{MI} [K]	*Structure*	*Reference*
TTF–TCNQ	600	53, 38	D, A	937–939
DTDSF–TCNQ	550	45	D, A	221, 940
TSF–TCNQ	800	28	D, A	399, 940, 941
TMTTF–TCNQ	600	34	D, A	942, 943
TMTSF–TCNQ	1000	57	D, A	944, 945
HMTTF–TCNQ	500	50, 43	D, A	946
HMTSF–TCNQ	1800	No	D, A	947, 948
HMTTeF–TCNQ	550		D, A	935
OMTTF–TCNQ	10^{-5}	–	DA	170, 949
TTF–TNAP	40	185	D, A	950
HMTSF–TNAP	2400		D, A	951, 952
TMTTF–TCNTP	0.2[a]			953, 954
DBTTF–TCNQ	10^{-7}	–	DA	172,192, 955
DBTTF–2,5-TCNQF$_2$	10^{-6}	–	DA	955
DBTTF–2,5-TCNQCl$_2$	40	180	D, A	956, 957
DBTSF–TCNQ	2.3×10^{-6}	–	DA	426
DBTSF–2,5-TCNQCl$_2$	20		D, A	426
TTF–chloranil	8×10^{-4}	–	DA	958, 959
TTF–Br	10^{-6}	–	DD	881
TTF–Br$_{0.76}$	500	180	D	881, 960, 961
(TMTTF)$_2$ClO$_4$	30	70	D	962–964
(TMTSF)$_2$ClO$_4$	500	No	D	965–967
(BEDT–TTF)$_2$ReO$_4$	200	81	D	968, 969
(BEDT–TTF)$_2$I$_3$	250	No	D	970–972
(BEDT–TTF)$_2$AuI$_2$		No	D	973

[a]compressed pellet, D donor stack, A acceptor stack, DA mixed stack, DD donor dimmers, DTDSF dithiadiselenafulvalene, TTF tetrathiafulvalene, TSF tetraselenafulvalene, TMTTF tetramethyltetrathiafulvalene, HMTTF and HMTSF and HMTTeF, respectively; hexamethylenetetrathiafulvalene, -tetraselenafulvalene, and –tetratellurafulvalene, respectively; OMTTF octamethylenetetrathiafulvalene, DBTTF and DBTSF, respectively; dibenzotetrathiafulvalene and -tetraselenafulvalene, respectively,; TNAP 11,11,12,12-tetracyano-2,6-napththoquinodimethane, TCNTP 13,13,14,14-tetracyano-4,5, 9,10-tetrahydro-2,7-pyrenoquinodimethane, 2,5-TCNQF$_2$ and TCNQCl$_2$, respectively; 2,5-difluoro- and 2,5-dichlorotetracyano-quinodimethane, respectively.

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 [974–979].

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 print circuit. During the metal deposition the organic layer is simultaneously removed, which results in a high adhesion of the metal image to the surface [893,894,980].

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 [981].

The TTF–TCNQ complex or TTF is used as electron transfer mediator in polymer coated electrodes for amperometric sensors of biologically important species, e.g. choline, acetylcholine [982–985], glucose [986–991], L-glutamic acid [992], NADH, uric acid, xanthine, 6-mercaptopurine, 6-thioxanthine, ascorbic acid [983]. Analogously the hexamethylenetetratellurafulvalene–TCNQ complex is a suitable electrode material for the amperometric detection of such species (e.g. glutathione, cysteine, ascorbic acid, NADH) [993].

Charge transfer complexes with TTF derivatives as donors form organic low-dimensional magnetic systems and provide a novel class of quantum spin systems that have never been known in ordinary inorganic magnetic systems [994].

7.3.3. Organic Superconductors

The intense effort to find new charge transfer salts with high conductivity and metallic properties led to the discovery of superconductivity in these radical salts. First of all in the tetramethyltetraselenafulvalenium salt $(TMTSF)_2\ ClO_4$ high conductivity was observed down to low temperatures and transition to the superconducting state (1.4 K) at ambient pressure [965]. Since then many charge transfer complexes with tetrachalcogenafulvalenes as donors have been prepared in the hope of finding new organic conductors or even superconductors. Superconductivity has been observed in a complex with the unsymmetrically substituted TTF derivative MDT–TTF, in complexes with the DTDSF derivative DMET and in a complex with $Ni(dmit)_2$ as acceptor (Table IX). However, the highest temperature T_c for the transition of an organic conductor to an organic superconductor is observed with BEDT–TTF salts, a selection of which can be found in Table IX.

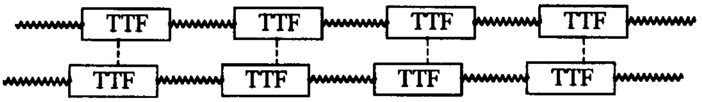
Also in a complex with the oxygen-containing donor BEDO–TTF superconductivity at ambient pressure has been found.

8. 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. The TTF moiety can be incorporated in a polymer chain in the following ways.

(a) Main-chain polymer

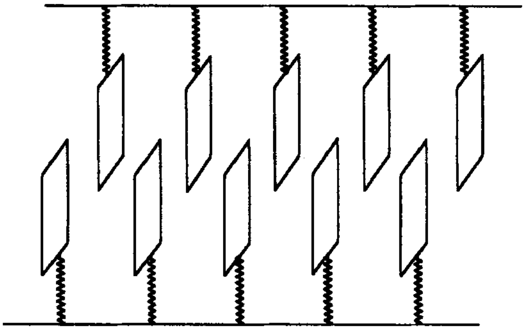
The TTF moiety is a part of the polymer chain and the TTF units are connected by flexible spacers. The TTF units in adjacent polymer chains form stacks with π-interaction.



SCHEME 230

(b) Side-chain polymer

The TTF moiety is attached at a polymer backbone and the TTF units can form stacks along the polymer chain with intramolecular interaction. Between neighbouring stacks a intermolecular interaction is possible.



SCHEME 231

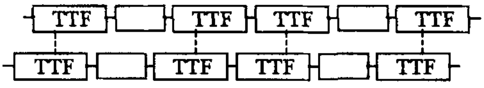
TABLE IX Organic superconductors and their transition temperature T_c to superconductivity

Complex	T_c *[K]	*References*
$(TMTSF)_2ClO_4$	1.4	965
$(TMTTF)_2Br$	0.8 (26 kbar)	995
$(MDT\text{-}TTF)_2AuI_2$	3.5	996
$(DMET)_2AuCl_2$	0.83	997
$(DMET)_2AuBr_2$	1.9	998
$(DMET)_2AuI_2$	0.55 (5 kbar)	997
$(DMET)_2Au(CN)_2$	1.1 (2.5 kbar)	999
$(DMET\text{-}TSF)_2AuI_2$	0.58	1000
$TTF[Ni(dmit)_2]_2$	1.6 (7 kbar)	1001
$(BEDT\text{-}TTF)_2ReO_4$	2 (4 kbar)	1002
$\beta\text{-}(BEDT\text{-}TTF)_2I_3$	1.5	970
	8 (1.3 kbar)	1003
$\kappa\text{-}(BEDT\text{-}TTF)_2I_3$	3.6	1004
$\theta\text{-}(BEDT\text{-}TTF)_2I_3$	3.6	1005
$(BEDT\text{-}TTF)_2IBr_2$	2.5	1006
$(BEDT\text{-}TTF)_2AuI_2$	3.8–5	973
$(BEDT\text{-}TTF)_2(I_3)_{2.5}$	2.5	1007
$\alpha\text{-}(BEDT\text{-}TTF)_2(NH_4)Hg(SCN)_4$	0.8	1008
$(BEDT\text{-}TTF)_4Hg_3Cl_8$	1.8 (12 kbar)	1009
$(BEDT\text{-}TTF)_4Hg_3Br_8$	4.3	1010
$(BEDT\text{-}TTF)_3Cl_2(H_2O)_2$	2.0 (16 kbar)	1011
$(BEDT\text{-}TTF)_4Pt(CN)_4(H_2O)$	2.0 (6.5 kbar)	1012
$(BEDT\text{-}TTF)_4Pd(CN)_2(H_2O)$	1.2 (7 kbar)	1013
$(BEDT\text{-}TTF)_2Ag(CN)_2(H_2O)$	5.0	1014
$(BEDT\text{-}TTF)_2Cu(NCS)_2$	10.4	1015
$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$	11.6	1016
$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$	12.5 (0.3 kbar)	1017
$(BEDT\text{-}TTF)_2Cu[N(CN)_2]CN$	11.2	1018, 1019
$(BEDT\text{-}TTF)_2Cu_2(CN)_3$	3.8	1017, 1019
$(BEDT\text{-}TTF)_2Cu(CF_3)_4(TCE)$	4.0	1020
$(BEDT\text{-}TTF)_2Cu(CF_3)_4(TCE)_X$ ($X < 1$)	9.2	1021
$(BEDT\text{-}TTF)_2Ag(CF_3)_4(TCE)$	11.1	1022
$(BEDO\text{-}TTF)_3Cu_2(NCS)_3$	1.06	1023

*unless otherwise noted, T_c is at ambient pressure, MDT–TTF methylenedithiotetrathiafulvalene, DMET dimethyl(ethylenedithio)ehtrathiafulvalene, DMET–TSF dimethyl(ethylenedithio)tetraselenafulvalene, TMTTF and TMTSF, respectively, tetramethyltetrathiafulvalene, -tetraselenafulvalene, respectively, BEDT–TTF and BEDO–TTF, respectively; bis(ethylenedithio) and bis(ethylenedioxo)tetrathiafulvalene, respectively; dmit dimercaptoisotrithione or 1,3-dithiole-2-thione-4,5-dithiolate.

(c) Conjugated polymer

The TTF moiety is part of the polymer chain and the TTF units are conjugatively connected. A π-conjugation along the polymer chain and an intermolecular π-interaction between neighbouring chains is possible.



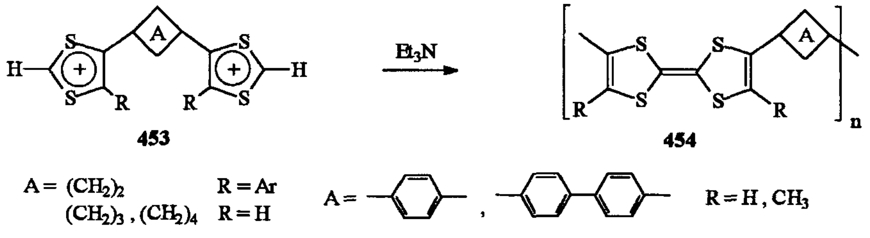
SCHEME 232

Forming of stacks of the donor units or π-interaction between donor units in the chains of polymers is a prerequisite to high mobility of electrons and with it to high conductivity of polymers after partial oxidation of the donor units by dopands or electrochemical oxidation. In main chain or side-chain polymers ordering of TTF units in stacks for a large extension is difficult to attain. Liquid-crystalline phases of polymers or stretch orientation of polymer films can promote this ordering.

Many polymers with tetrathiafulvalene units in the above three arrangements have been prepared by different synthetic methods.

8.1. Deprotonation of Bis(1,3-dithiolium) Salts

In a manner analogous to the synthesis of 1,3-dithiolium salts (see Section 1.2) the bis(1,3-dithiolium) salts **453** can be synthesized and converted with tertiary aliphatic amines (e.g. triethylamine) in acetonitrile or acetone to the polymeric TTF **454** [1024–1027]. Terminal group analysis showed that the molecular weight (M_n) of the polymeric TTF **454** was about 2000–4000. The polymers **454** 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 **454** only to the monocations of the TTF unit which can be characterized ESR spectroscopically via a structureless signal [1025–1027]. Iodine or TCNQ converts the polymeric TTF **454** 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 [1027]. Because of the insolubility of 4,4′-bis(1,3-dithiolium) perchlorate it was not possible to couple it to the corresponding polymer [1028].

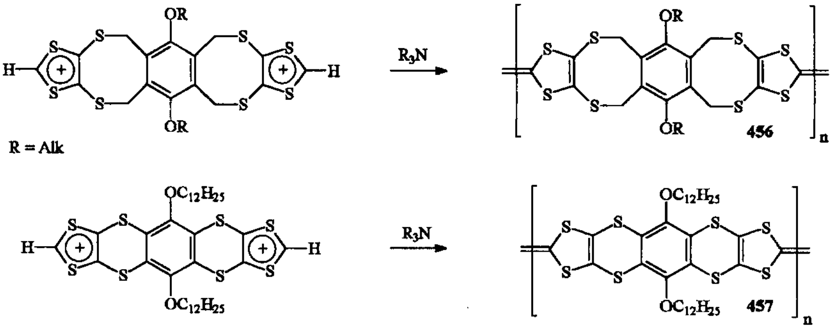


SCHEME 233

Deprotonation of the corresponding bis(1,3-dithiolium) salt provides the planar and conjugatively connected polytetrathiafulvalene **455**. This polymer reacts with bromine, iodine or TCNQ and forms radical cation salts with an electrical conductivity of up to $3 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ [1029]. The radical cation salts of **455** show a higher conductivity than twisted phenylene-bridged polymeric radical cation salts **454** [1029–1031]. The oxidation of the polymer **455** with bromine or iodine leads to the generation of charge carriers (polarons, bipolarons) which are responsible for conductivity [1032,1033].

SCHEME 234

The poor soluble, fully conjugated polymers **456** ($n = 6$) and **457** are formed by deprotonation of the corresponding bis(1,3-dithiolium) salts with diisopropyl(ethyl)-amine [1034]. After doping with iodine the black-coloured polymer **457** exhibits no electrical conductivity, probably only the surface of the particles is doped [1035].



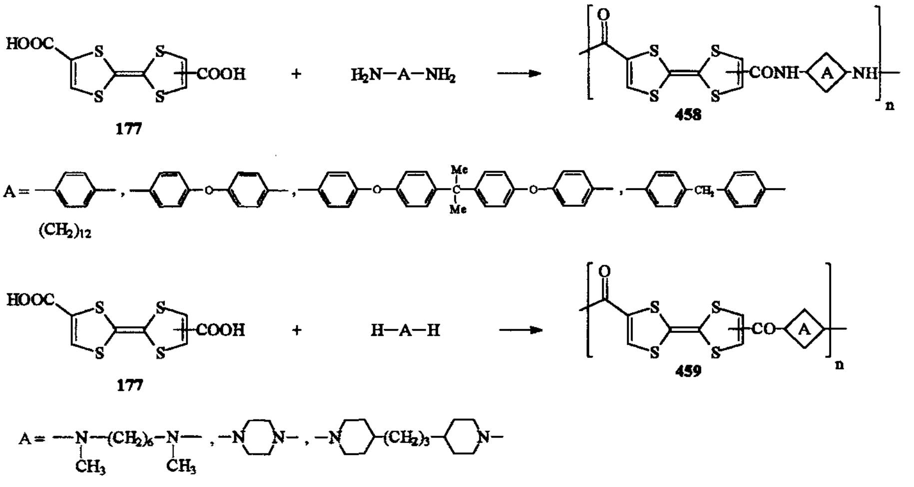
SCHEME 235

Polymeric TTF **454** 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 [1036].

Polymeric TTF **454** are also 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 [1037].

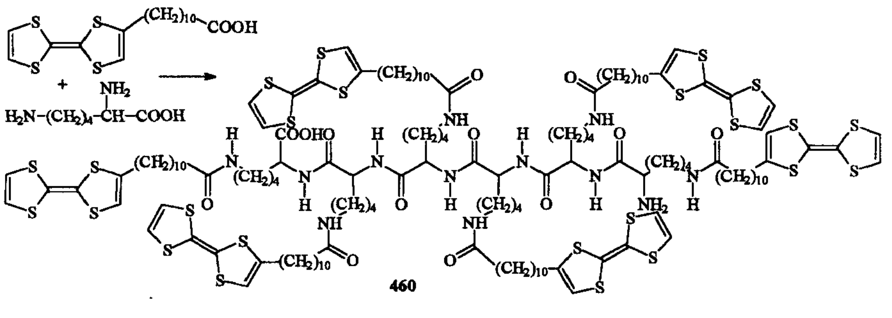
8.2. Polycondensation of Tetrathiafulvalene Derivatives

Bivalent tetrathiafulvalene derivatives condense with bivalent amines, alcohols, carboxylic acids, isocyanates, or sulfonyl chlorides to form polyamides [1038–1040], polyesters [1041,1042], polyurethanes [1043,1044], and polysulfonates [1044], respectively. The polycondensation of the diacid **177** with amines is readily effected in *N*,*N*-dimethylformamide at 70°C with diphenyl phosphite/pyridine [1038] or in pyridine with triphenylphosphine/hexachloroethane [1039] as dehydration reagent. The polyamides **458** and **459** are only soluble in trifluoroacetic acid, hexamethylphosphoramide, or dimethyl sulfoxide. With TCNQ they do not form charge transfer complexes [1038]. With bromine the tetrathiafulvalene unit is oxidized to the monocation, causing an increase in the conductivity ($\sigma_{RT} \leq 10^{-5}\,\mathrm{S\,cm^{-1}}$) [1039].



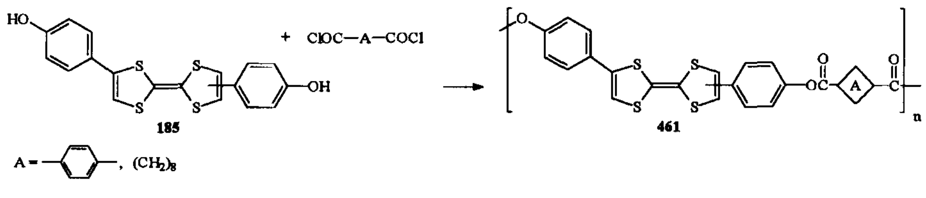
SCHEME 236

A polypeptide **460** with attached tetrathiafulvalene units has also been prepared [1040].



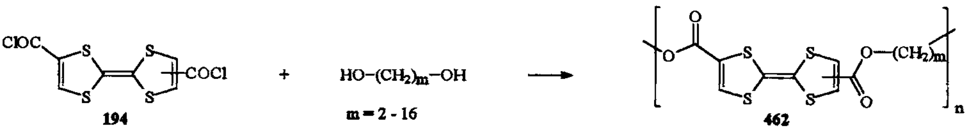
SCHEME 237

The polyesters **461** 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 [1041].



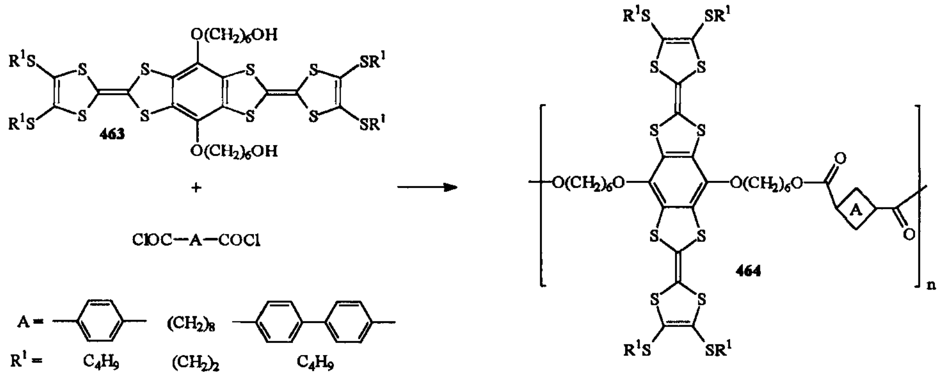
SCHEME 238

The polyesters **462** (n: 3–5; M_n 2000) are insoluble in organic solvents. Upon grinding of the polyesters **462** with TCNQ their conductivity is enhanced by one to five orders of magnitude ($\sigma_{RT} \leq 10^{-7}\,\mathrm{S\,cm^{-1}}$) [1042].

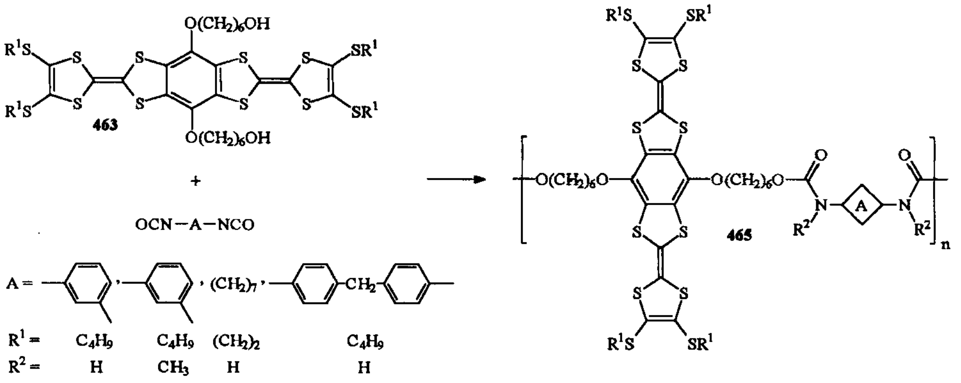


SCHEME 239

Polycondensation of the TTF **463** with diacid chlorides in dichloromethane provides polyesters **464**. TTF **463** reacts with diisocyanates in a polyaddition at 110°C, under an inert atmosphere in the absence of solvent, resulting in orange-coloured polyurethanes **465**, which are highly soluble in dichloromethane. The polymers **464** and **465** exhibit a glass transition point and a melting point, but no liquid-crystalline phase. After doping of the polyurethane **465** (A = 1,3-phenylene, $R^1 = C_4H_9$, $R^2 = H$) with $TCNQF_4$ a free-standing film can be cast from 1,1,2,2-tetrachloroethane solution with a conductivity of $8 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ [1035].

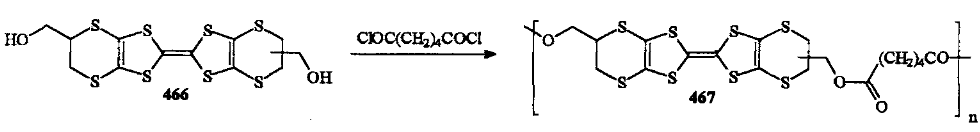


SCHEME 240



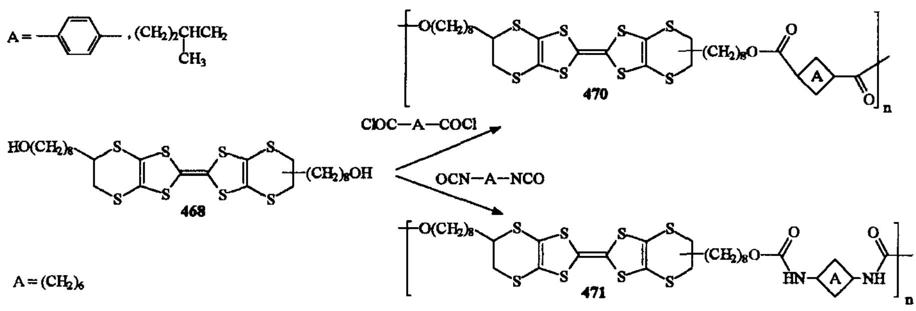
SCHEME 241

The bis(ethylenedithio)-TTF derivative **466** provides with butanedioyl dichloride the polymer **467**, soluble in *N*-methylpyrrolidone, DMF and DMSO. After oxidation with TCNQ or iodine the conductivity of **467** is increased to $5 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$. The conductivity of casted polymer films of **467** is increased from 3.4×10^{-15} to $2.2 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$ after iodine doping [1045].

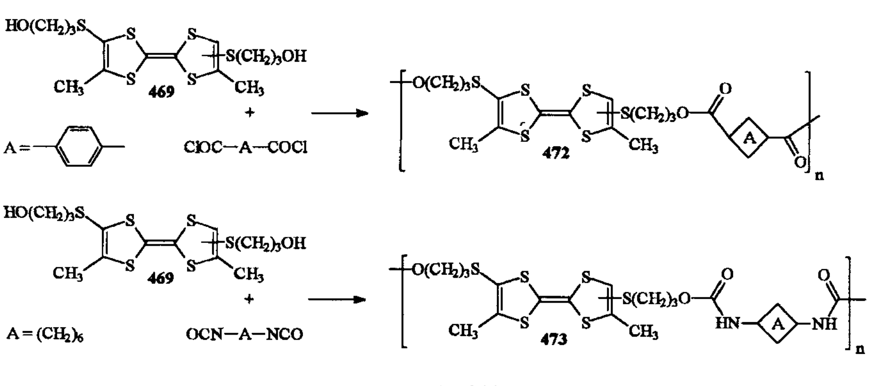


SCHEME 242

TTF **468** and **469** yield with diacid chlorides or diisocyanates polyesters **470**, **472** or polyurethanes **471**, **473**, respectively, which are soluble in common organic solvents [1046–1048]. Polymers **470** and **471** display well resolved cyclic voltammograms in dichloromethane, quite similar to BEDT–TTF. Transparent free-standing films can be cast from solution. The films of polymers **470** and **471** show after oxidation with iodine or $Fe(ClO_4)_3$ electrical conductivity ranging from 5×10^{-3} [**470**, $A = (CH_2)_2CH(CH_3)CH_2$] to $2 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$ (**470**, A = 1,4-phenylene). After stretch orientation and doping with iodine the conductivity perpendicular to the stretch axis was greater than parallel to the stretch axis. This suggests preferential ordering of the TTF units in stacks.

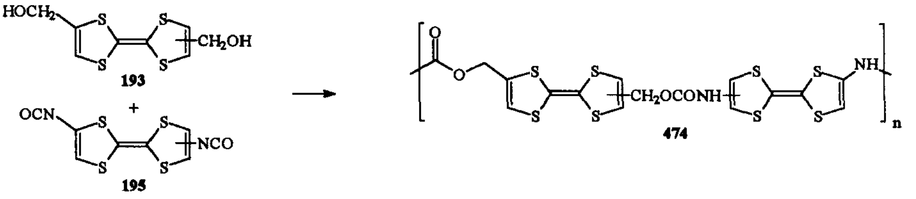


SCHEME 243



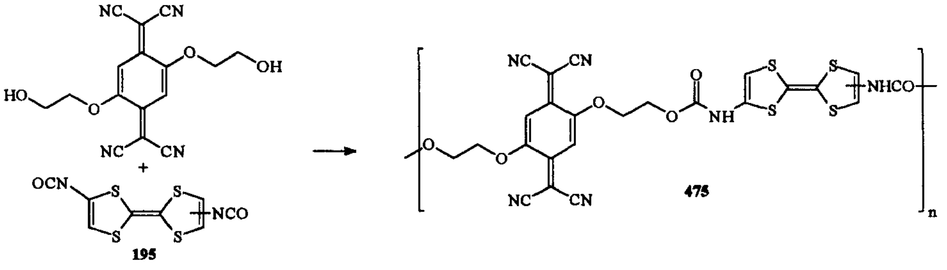
SCHEME 244

The brown polyurethane **474** is insoluble, but can be oxidized with iodine, whereby the conductivity increases by two orders of magnitude ($\sigma_{RT} = 2 \times 10^{-6}\,S\,cm^{-1}$) [554].



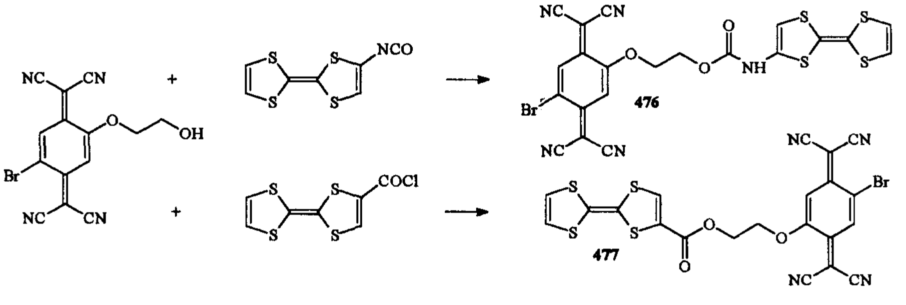
SCHEME 245

In the same manner a charge transfer polymer **475** containing covalently bound TCNQ has been prepared. The black polyurethane **475** is amorphous and possesses an electric conductivity of $1.7 \times 10^{-7}\,S\,cm^{-1}$ [554].



SCHEME 246

The monomers **476** and **477** of similar structure have also been synthesized. Both appear to be zwitterionic [555].

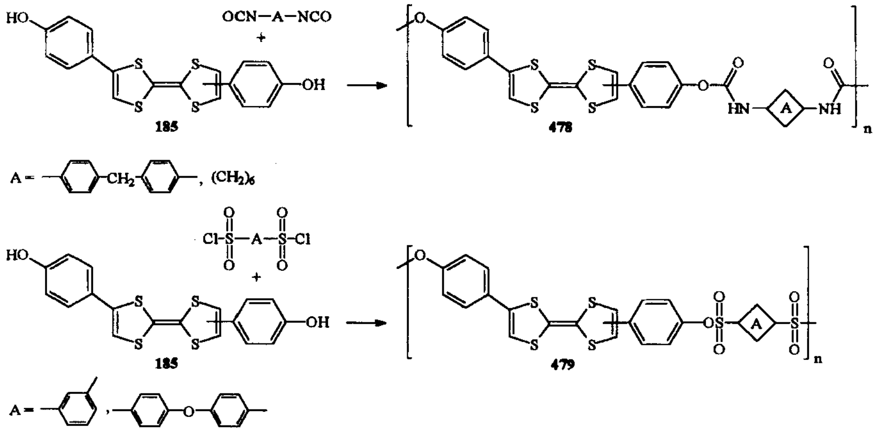


SCHEME 247

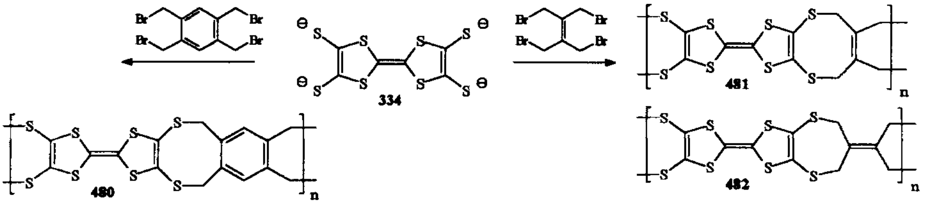
The polyurethanes **478** as well as the polysulfonates **479** are readily soluble in trifluoroacetic acid at room temperature and in *N*,*N*-dimethylformamide, dimethyl sulfoxide, and hexamethylphosphoramide upon heating. They form no charge transfer complexes with TCNQ, but can be oxidized with bromine [1043].

TTF-tetrathiolate **334**, synthesized by deprotection of tetrakis(cyanoethylthio)-tetrathiafulvalene with sodium ethoxide, provides with tetrabromoderivatives polymeric TTF **480** or **481** which are insoluble in common solvents. Elemental analysis shows the bromine content to be less than 4% demonstrating the polymeric character

($n = 8$–16). A comparison of the IR spectra of **481** and the corresponding monomer gives evidence for the formation of **481** and not **482** with seven-membered dithiole ring or a polymer having a statistical mixture of the two geometries. Doping of the polymers **480** and **481** increases the electrical conductivity to 2×10^{-4} and $6 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$, respectively [1049].

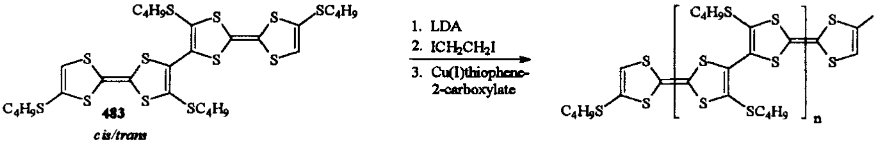


SCHEME 248



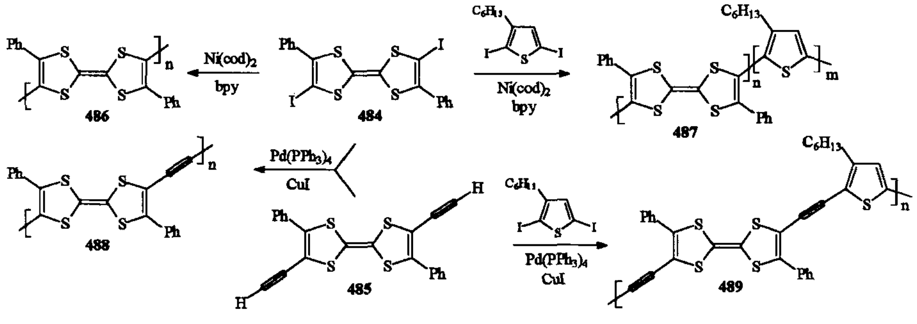
SCHEME 249

Lithiation of the TTF dimer **483** with LDA followed by iodination with 1,2-diiodoethane provides a mixture of iodo derivatives, which are converted in an Ullmann coupling with excess copper(I)thiophene-2-carboxylate in 1-methyl-2-pyrrolidinone at room temperature to a mixture of oligomers. The mixture is separated by preparative gel-permeation liquid chromatography and affords oligomers up to the dodecamer, which form a film on ITO glass with electrochromic properties [1050].



SCHEME 250

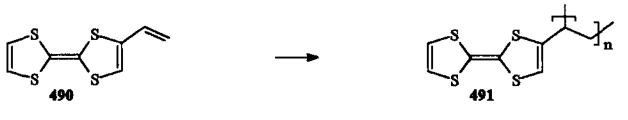
In a nickel-promoted polycondensation [Ni(cod)$_2$ = bis(cycloocta-1,5-diene)nickel(0), bpy = 2,2′-bipyridyl] of the 4,4′-diiodo-5,5′-diphenyl-TTF **484** or a 1 : 1 mixture of **484** and 2,5-diiodo-3-hexyl-thiophene in DMF at 50°C the polymers **486** and **487** are formed in 100 and 85% yields, respectively, where the GPC for **487** gives M_n 4700. The palladium-promoted polycondensation of a mixture of **484** and 4,4′-diethynyl-5,5′-diphenyl-TTF **485** or **485** and 2,5-diiodo-3-hexyl-thiophene in THF/Et_3N at 60°C provides the polymers **488** and **489** in 93 and 100% yield, respectively. Polymers **488** and **489** are partly soluble in THF and the THF soluble part gives M_n 2320 and 610000, respectively. Polymers **488** and **489** show electrical conductivities of 2.1×10^{-7} and $8.5 \times 10^{-8}\,S\,cm^{-1}$, respectively, which raises after doping with iodine of 4.7×10^{-3} and $2.7 \times 10^{-4}\,S\,cm^{-1}$, respectively, at rt [1051].



SCHEME 251

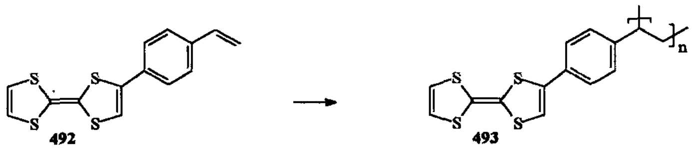
8.3. Polymerization of Tetrathiafulvalene Vinyl Monomers

Tetrathiafulvalene vinyl monomers can be polymerized under various reaction conditions. The vinyltetrathiafulvalene **490** can be polymerized thermally as well as by UV initiation, azobisisobutyronitrile, or by adding TCNQ, and forms low-molecular weight polymers **491**. This polymer **491** forms charge transfer complexes with bromine or TCNQ [624]. Copolymerization of equimolar amounts of a vinyl or allyl substituted TTF and a vinyl or allyl substituted TCNQ in the presence of an azo or peroxide catalyst provide thermoplastic polymers with electroconductive properties [1052].



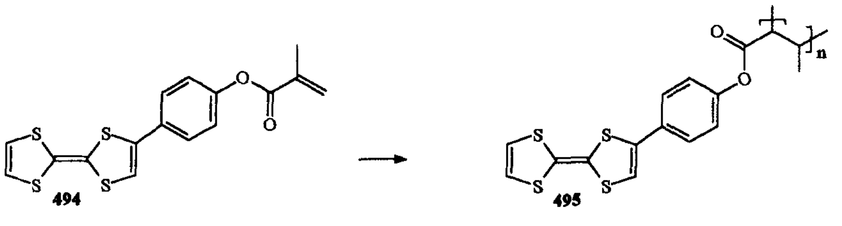
SCHEME 252

The polymerization of 4-(4-vinylphenyl)tetrathiafulvalene **492** was carried out in a sealed tube *in vacuo* at 130°C for 3 days. A polymer **493** with a molecular weight of about 50000 was isolated. The brown polymer **493** is insoluble in all usual organic solvents. With bromine the polymer **493** is oxidized and its conductivity increases by two orders of magnitude to $10^{-8}\,S\,cm^{-1}$. Attempted anionic polymerization or initiation with azobisisobutyronitrile was unsuccessful [1053].



SCHEME 253

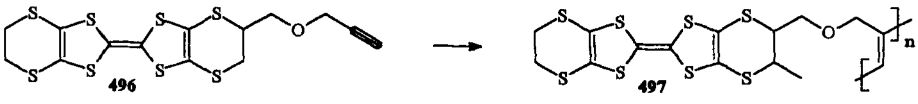
The polymerization of 4-(tetrathiafulvalen-4-yl)phenyl methacrylate **494** is only successful in a sealed tube *in vacuo* upon heating at 120°C for 2 days. The black polymer **495** is only soluble in strong acids. It is converted with bromine into a bromine complex. The copolymerization with methyl methacrylate gives a soluble copolymer with a molecular weight (M_n) of about 10 000 (93,5% of MMA) [551].



SCHEME 254

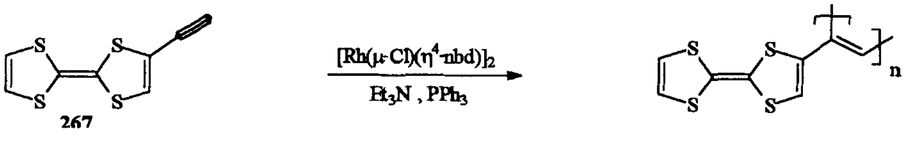
8.4. Polymerization of Tetrathiafulvalene-substituted Alkynes

An alkyne **496** substituted by a tetrathiafulvalene derivative gives after polymerization a polyalkyne **497** containing tetrathiafulvalene side groups. The polymer doped with iodine vapour or iodine solution shows electrical conductivity of 1.95×10^{-5} or $7.3 \times 10^{-9}\,\mathrm{S\,cm^{-1}}$, respectively [1054].



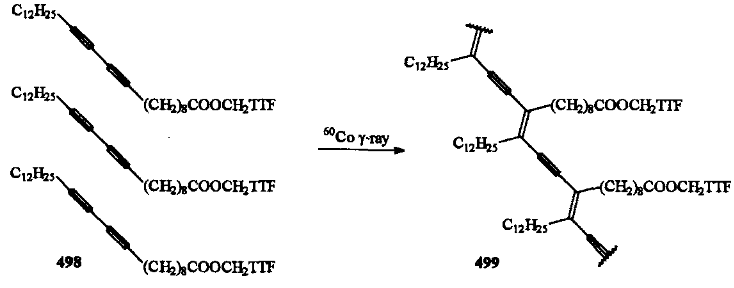
SCHEME 255

Polymerization of 4-ethynyltetrathiafulvalene **267** is carried out by using $[\mathrm{Rh}(\mu\text{-Cl})(\eta^4\text{-nbd})]_2$ (nbd = norbornadiene) as catalyst and triethylamine as cocatalyst, modified by triphenylphosphine, at rt in THF and dark-brown powder of poly(4-ethynyltetrathiafulvalene) is obtained. In dependence of the reaction conditions (concentration of catalyst, reaction time, addition of triphenylphosphine, without solvent) polymers with different number average molecular weight (M_n) of 6000–11 700 are formed which are soluble in polar solvents. After reaction with acceptors the electrical conductivity of the polymer ($\sigma_{RT} < 10^{-9}\,\mathrm{S\,cm^{-1}}$) is increased and shows with TCNQ (molar ratio 5 : 1) the highest electrical conductivity ($\sigma_{RT} = 2.1 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$) [1055].



SCHEME 256

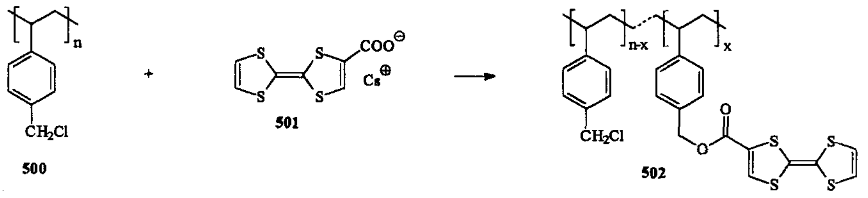
The diacetylene **498** with a tetrathiafulvalene unit in the side chain is readily polymerized in the solid state stimulated by ^{60}Co γ-ray irradiation. The polymer **499** is insoluble in benzene. According to solid state high resolution ^{13}C NMR measurements the spectrum is consistent with the structure of **499** [1056,1057].



SCHEME 257

8.5. Reactions of Polymers

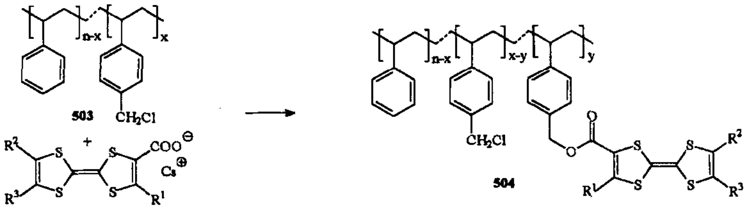
Another polymeric tetrathiafulvalene is formed by reaction of a linear poly[4-(chloromethyl)styrene] **500** with the cesium salt of carboxytetrathiafulvalene **501**, where 30% of the sites have reacted with the tetrathiafulvalene moiety. The tetrathiafulvalene substituted polystyrene **502** is soluble in tetrahydrofuran and films can be prepared [1044].



SCHEME 258

Such a polystyrene derivative with attached tetrathiafulvalene units is useful as a negatively working photoresist. X-ray or e-beam exposure 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 [1058–1060].

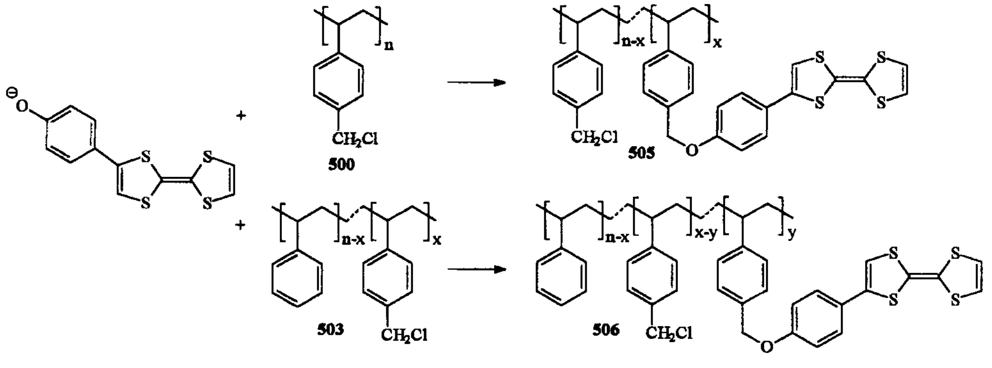
The poly[4-(chloromethyl)styrene] **500** or the copolymer poly-[styrene-*co*-4-(chloromethyl)styrene] **503** with a variety of controlled molecular weights and molecular weight distribution react with cesium tetrathiafulvalenecarboxylate and proceeds new polystyrenes **502** or **504**, respectively, bearing tetrathiafulvalene units attached to the backbone [1061,1062]. The resists show under electron beam irradiation in the presence of dibromotetrachloroethane good properties as negative resists, including high sensitivity, no swelling and high resolution [1063–1065].



SCHEME 259

Analogous to the polymer **500** a polymer backbone with attached tetrathiafulvalene units has been prepared by reaction of poly[4-(chloromethyl)styrene] **500** or poly-[styrene-*co*-4-(chloromethyl)styrene] **503** with potassium 4-tetrathiafulvalenylphenoxide.

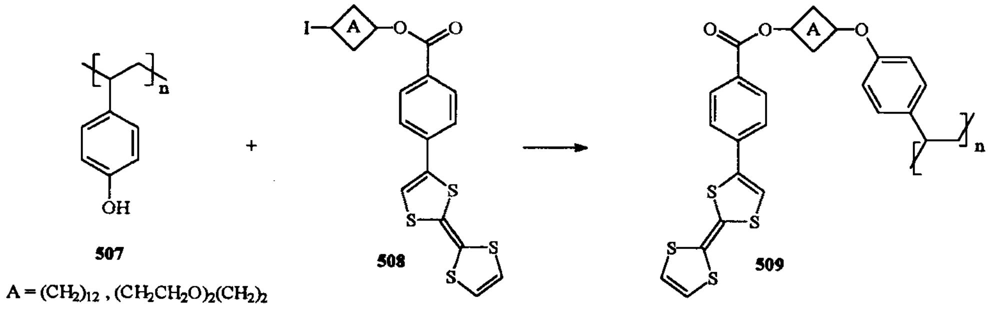
The TTF-substituted polystyrene copolymer **505** (70% of the the sites are substituted by the TTF moiety) is soluble in tetrahydrofuran, *N*,*N*-dimethylformamide, dichloromethane, and insoluble in acetonitrile. It can be cast onto electrode surfaces to form stable films, which are able to transport electrons and counterions through the polymer matrices in electrochemical processes [838,1066].



SCHEME 260

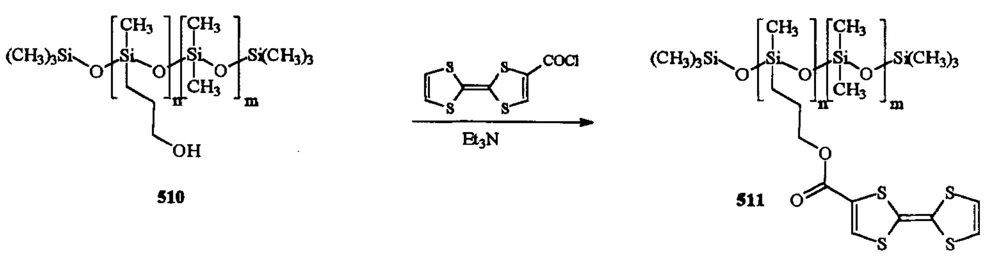
Other authors prepared the polymers **505** and **506** with a variety of controlled molecular weights and molecular weight distributions, which differ in their solubilities. Whereas polymers **505** are highly insoluble, the polymers **506** are soluble in dichloromethane. The suitability of the polymers **505** and **506** for microlithographic processes is being studied [1064,1065,1067].

Deprotonation of poly(4-hydroxystyrene) **507** with potassium carbonate in *N*,*N*-dimethylformamide and further reaction with the TTF derivatives **508** provide orange-coloured polymers **509**, which are soluble in common organic solvents and can be cast to films [1035]. The polymers exhibit no liquid-crystalline phase. After doping with DDQ, $TCNQF_4$ or iodine the complexes show a low conductivity ($\sigma_{RT} = 10^{-9}\,S\,cm^{-1}$).



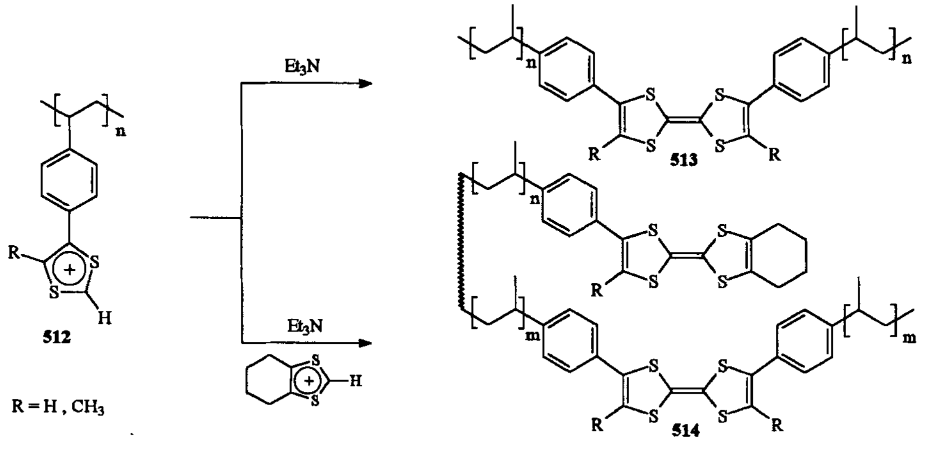
SCHEME 261

The TTF containing siloxane polymer **511** was prepared by esterification of the polymer **510** with tetrathiafulvalene–carbonyl chloride in the presence of triethylamine. The insoluble gummy polymer **511** can effectively mediate electron transfer from the reduced flavin adenine dinucleotide redox centers of glucose oxidase to a conventional carbon paste electrode [986]. A covalently attached TTF derivative to the glucose oxidase is also used as a mediator for the oxidation of the enzyme [1068].



SCHEME 262

Tetrathiafulvalene substituted polystyrenes **513** and **514** are also obtained by acylation of an atactic polystyrene (M_n 3200) with α-halo acid halides and further conversion to the corresponding dithiolium salts **512**, which are further treated with triethylamine [1069]. These polymers **513** and **514** 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} S cm^{-1}) [1069].

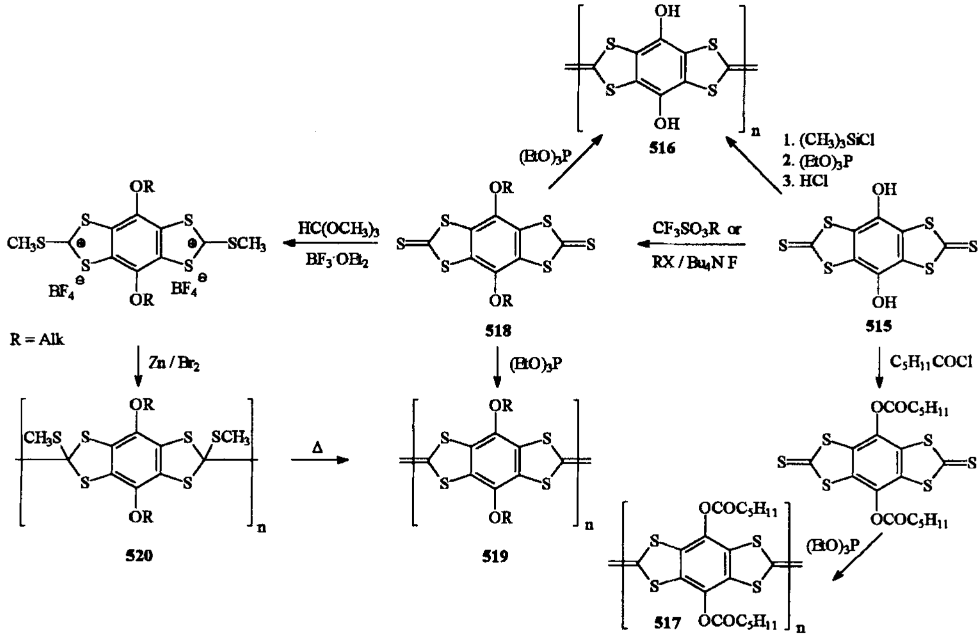


SCHEME 263

8.6. Miscellaneous Methods

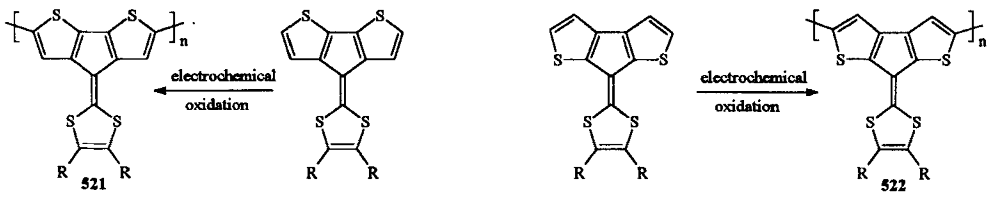
The reaction of dithione **515** with triethyl phosphite yields a black insoluble polymer, presumably **516**, which could not be characterized. The same product was also achieved by silylation of **515** with trimethylsilyl chloride, subsequent coupling with triethyl phosphite and hydrolysis with dilute hydrochloric acid. Pressed pellets of the polymer show an electrical conductivity of about 10^{-2} S cm^{-1}, which increased up to two orders of magnitude upon exposure to iodine vapour. After acylation of **515** with hexanoyl chloride the dithione formed gives with triethyl phosphite a slightly soluble dark reddish-brown polymer presumably with the structure **517** [821].

Coupling of the dithiones **518** with triethyl phosphite provides the polymers **519** ($n = 15$–20), which show after doping with iodine a conductivity of $\sigma_{RT} = 2 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ [1034]. Alkylation of the dithione **518** ($R = C_6H_{13}$) and subsequent reduction with zinc is a better method of polymerization and leads to high molecular weights and processable polymers **520**. These polymers were cast on a glass plate and by thermal extrusion of dimethyldisulfide the conjugated polymer **519** is formed, where after doping with iodine the highest conductivity ($0.55\,\mathrm{S\,cm^{-1}}$) is measured with an iodine content (I_3^-) of 60% [1070].



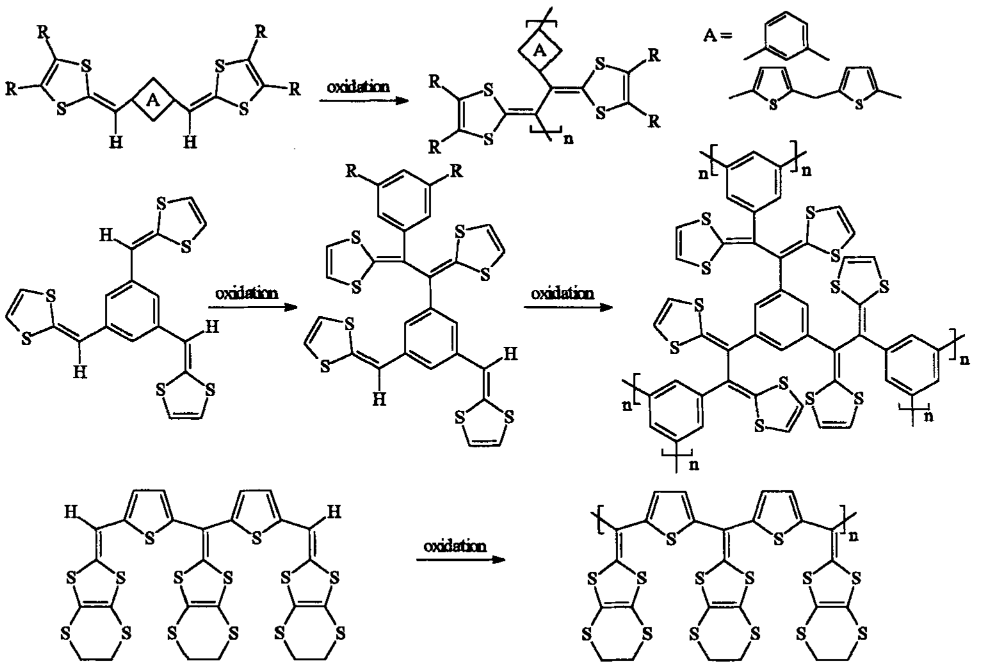
SCHEME 264

Polymers with 1,3-dithiol-2-ylidene units have also been formed by electrolytic oxidation of the corresponding 1,3-dithiole monomers. After electrical doping the polymer films exhibit electrical conductivity (in the range of 10^{-4}–$50\,\mathrm{S\,cm^{-1}}$ for polymer **521** and 10^{-3}–$10^{-2}\,\mathrm{S\,cm^{-1}}$ for polymer **522**) [1071].



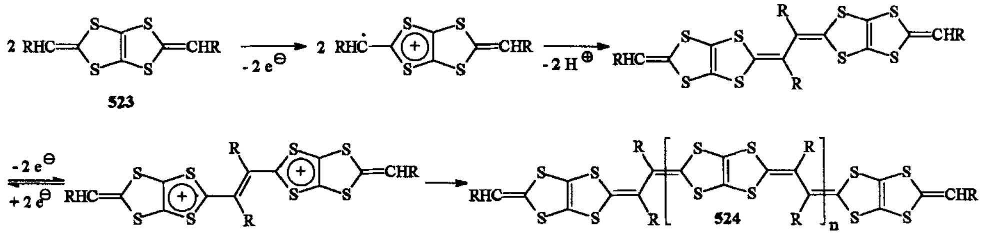
SCHEME 265

Molecules with more than one 1,4-dithiafulvene unit form polymers with ethanediylidene moieties upon electrochemical oxidation (in analogy to the electrochemical oxidation of 1,4-dithiafulvenes, but in contrast to 1,2-phenylenebis(1,4-dithiafulvenes), see Section 6) [451,484–486,1072–1074] or chemical oxidation with tris(4-bromophenyl)aminium hexachloroantimonate [1074].



SCHEME 266

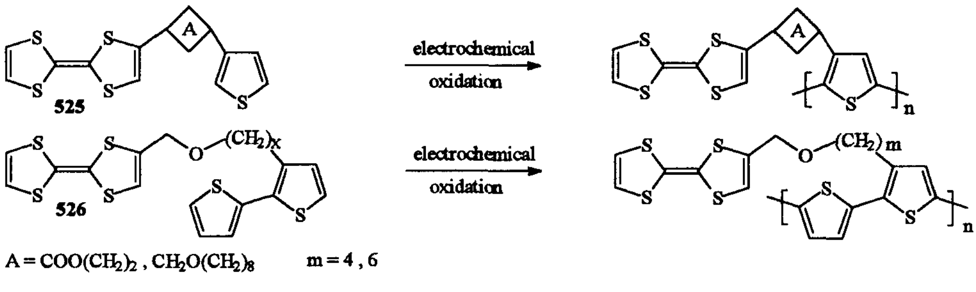
The bifunctional 1,3,4,6-tetrathiapentalenes **523** are electrochemically oxidized and provide upon continued potential cycling in a stepwise construction the extended, vinylogous TTF **524** (in analogy to the electrochemical oxidation of 1,4-dithiafulvenes, see Section 6) [1075–1077]. The obtained films by electropolymerization exhibit conductivities of 10^{-1}–1 $\mathrm{S\,cm^{-1}}$ [1078]. In the case of R = Ph a vinylogous, linearly fused TTF polymer is formed, consisting of eight monomer units. The prepared films are stable and show a pronounced electrochemical reversibility by continued potential cycling (500 cycles) in solution between 0 and 0.75 V [1079].



SCHEME 267

TTF systems covalently linked by a linear oxydecyl or carbonyloxyethyl spacer to a thiophene ring in the 3-position are synthesized. Electropolymerization of the thiophene **525** (A = $COOCH_2CH_2$) [1080] to a polythiophene derivative in nitrobenzene/dichloromethane solution provides an orange deposit at the anode but the electropolymerization of the thiophene **525** [A = $CH_2O(CH_2)_8$] [842] in acetonitrile is unsuccessful, presumably because of the scavenging of the thiophene cation radicals by TTF, but can be achieved by application of repetitive potential scans in nitrobenzene solution. In agreement with UV–Vis absorption spectra the formation of a donor acceptor complex between nitrobenzene and the TTF moiety decreases its reactivity toward thiophene cation radicals and enables polymerization. 2-Thienyl [1081] or 3-thienyl [1082,1083] substituted TTF derivatives can not be electropolymerized under a variety of conditions. Although a blue coloration was generated in solution, it was not possible to grow polymer films. The generated tricationic species are unstable and react rather with the solvent or the anion, after diffusion away from the electrode surface to form by-products, than they polymerize at the electrode surface. Contrary a bis(3,4-ethylenedioxy-2-thienyl)TTF derivative is anodically polymerized in acetonitrile and provides a polythiophene product containing TTF moieties regularly inserted in the polythiophene chain [651].

The much lower oxidation potential of bithiophene compared to thiophene allows the facile electropolymerization of the TTF derivative **526** into electroactive polymers [651,1084–1086].

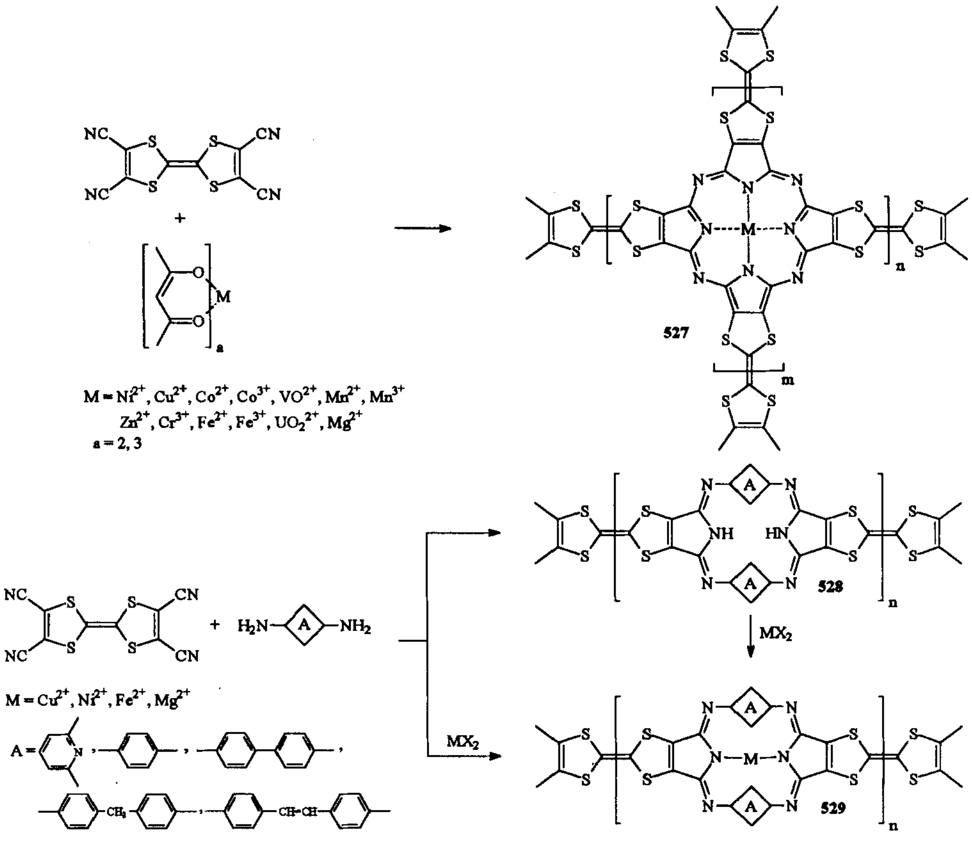


SCHEME 268

Thiophene, fused with a TTF-species, shows no polymerization under electrochemical conditions. Probably the TTF-unit leads to a stabilization of the radical cation within the thiophene part of the molecule [1083,1087]. However, a terthiophene-fused TTF derivative affords by electrochemical oxidation under identical conditions reproducible films of a polymer [1088].

The tetrakis(mercaptopropylthio)tetrathiafulvalene is electropolymerized at moderate potential into highly stable poly TTF films on metal electrodes by oxidation of the thiol groups [1089].

Tetracyanotetrathiafulvalene forms with metal acetylacetonates polymers with phthalocyanine-like structures **527** and with diamines polymers of the hemiporphyrazine type **528**, both containing tetrathiafulvalene units [1090,1091]. Both types of polymers **527** and **528** are dark coloured, insoluble in all solvents and show semiconductor properties ($\sigma_{RT} < 10^{-5}\,S\,cm^{-1}$). In the case of the hemiporphyrazine type polymers **528** the two hydrogen atoms inside the macroheterocyclic ring can be substituted by metal atoms to form **529**. Depending on the metal atom and the bridging group A the electric conductivity increases up to two orders of magnitude [1092].



SCHEME 269

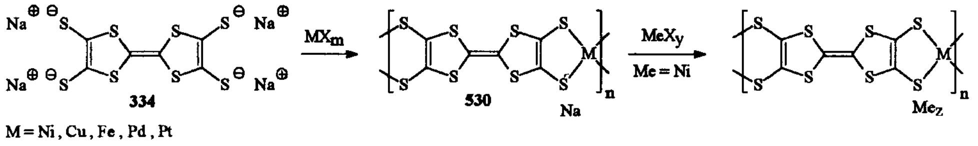
A polymer with bridged tetrathiafulvalene units by S–S linkages is formed by treatment of bis(tributylstannylthio) TTF **356** with gaseous hydrogen chloride (see Section 7.1) [194].

8.7. Polymeric Tetrathiafulvalene Metal Bisdithiolene Complexes

The reaction of tetrathiafulvalenetetrathiolate **334** with metal salts leads to the precipitation of insoluble, amorphous powders **530**, where the conductivity varies with the conditions of the synthesis, but the copper and nickel complexes show the highest conductivity (M: Cu $\sigma_{RT} = 10^{-1}\,\mathrm{S\,cm^{-1}}$, M: Ni $\sigma_{RT} = 30\,\mathrm{S\,cm^{-1}}$) [129,590,602,1066, 1093,1094]. Whereas addition of small amounts of a reducing agent during the synthesis of Cu or Ni polymer complexes slightly increases the conductivity, addition of an oxidant decreases the conductivity [1093]. On the contrary, other authors find an enhancement of the conductivity after chemical oxidation of the Ni polymer [1095,1096].

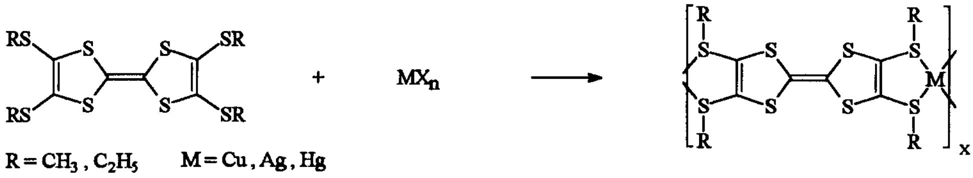
A ribbon structure, but also two-dimensional layers, could be formed. Qualitative MO and band structure calculations support this assumption [1092].

To study the influence of counter ions on the electrical conductivity of the nickel polymers, transition metal and lanthanide ions are introduced. The measured compaction powder conductivities are approximately similar, suggesting that the conductivity is not effected by counter ions [1097].



SCHEME 270

Tetrakis(alkylthio)–TTF forms with metal salts coordination polymer chains. The TTF derivative acts as a bridging chelate ligand and coordinated the metal ions by four S atoms. The complexes are insulators at room temperature but behave as semiconductors after doping with iodine (M = Cu, 2×10^{-3} S cm^{-1}) [1098–1102].

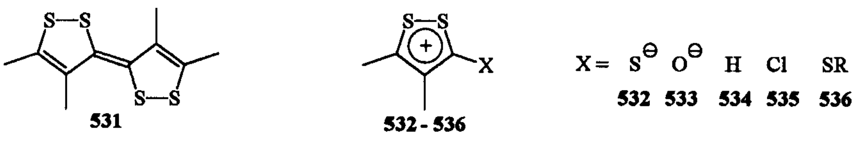


SCHEME 271

9. SYNTHESIS OF 1,2-TETRACHALCOGENAFULVALENES (1,2-TXF)

While the 1,3-tetrathiafulvalenes have been known for many years, especially since the discovery of the high electric conductivity of their charge transfer complexes, and many new and efficient syntheses have been described, the chemistry of the analogous 1,2-tetrathiafulvalenes **531** is poorly developed. The first synthesis of 1,2-TTF was reported in 1975 [1103].

Most pathways to 1,2-TTF start from the 1,2-dithioles **532–536**. In this report we are only reviewing some of the more common possibilities for the synthesis of these compounds (more detailed information has been published in review articles [179,181,1104–1109]).

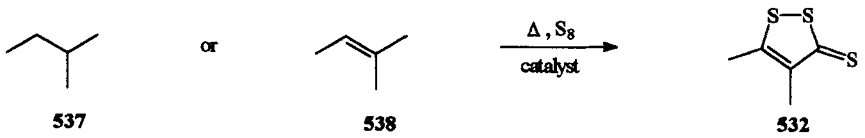


SCHEME 272

9.1. Synthesis of 1,2-Dithiole Derivatives

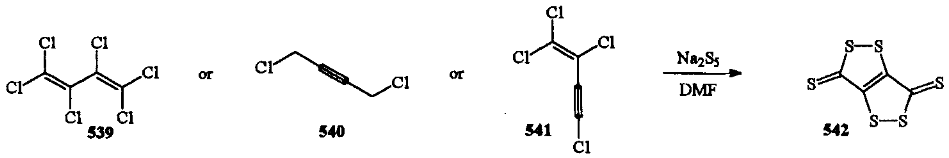
9.1.1. 1,2-Dithiole-3-thiones

1,2-Dithiole-3-thiones ('trithiones') **532** are available by high-temperature sulfurization (200–500°C) of the hydrocarbons **537** or **538** and their derivatives [1110]. The yields are good in some cases and can be increased by the use of basic catalysts (e.g. diphenylguanidine) [1111].



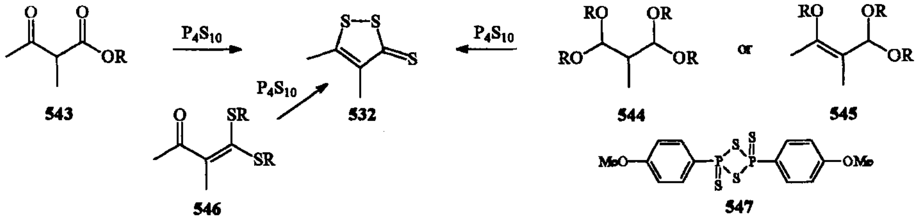
SCHEME 273

Polyhalogenated hydrocarbons can be thiated at lower temperatures in aprotic solvents (e.g. **539**–**542**) [1112].



SCHEME 274

A very efficient way to the trithiones **532** is the sulfurization of β-keto esters **543** and their functional derivatives (e.g. **544**–**546**) with phosphorus pentasulfide [1113,1114], preferably in the presence of sulfur [1115] or 2-mercaptobenzothiazole/zinc oxide as catalyst [1116]. In many cases the yields can be considerably increased by use of the 2,4-diphospha-1,3-dithietane **547** (Lawessons's reagent) as sulfurization agent [1117].



SCHEME 275

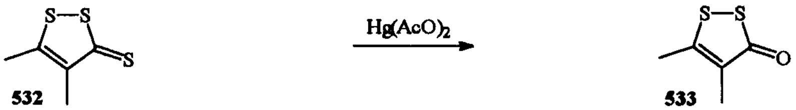
Another common way to trithiones **532** starts from the enamines **548**, carbon disulfide, and sulfur [1118].

SCHEME 276

The 4,5-dimercapto-1,3-dithiole-2-thione dianion **20** isomerizes to 4,5-dimercapto-1,2-dithiole-3-thione dianion at 120–140°C in dimethylformamide solution and can be isolated as the tetrabutylammonium zinc chelate, which is converted into 4,5-bis(benzoylthio)-1,2-dithiole-3-thione, then to 4,5-dimercapto-1,2-dithiole-3-thione dianion by cleavage with bases and afterwards by alkylation to 4,5-bis(alkylthio)-1,2-dithiole-3-thiones [1119].

9.1.2. 1,2-Dithiol-3-ones

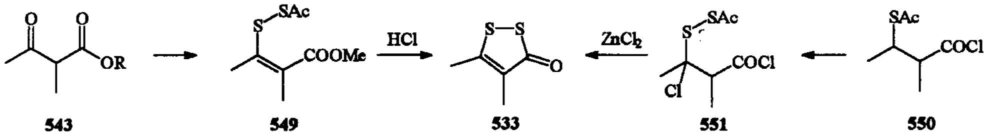
The 1,2-dithiol-3-ones **533** can be obtained from the corresponding 1,2-dithiole-3-thiones by desulfurization with mercury(II)acetate [222].



SCHEME 277

Furthermore, 1,2-dithiol-3-ones **533** 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 of up to 65% [1120].

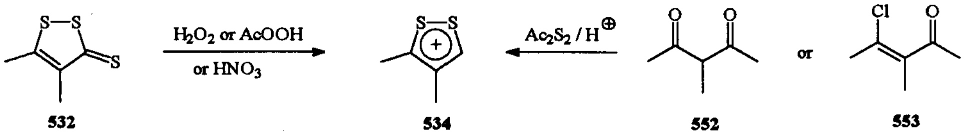
A common method used to obtain 1,2-dithiol-3-ones **533** starts from *β*-keto esters **543** and leads to the 1,2-dithiol-3-ones via the *β*-acetyldithioacrylic esters **549** [1121]. In a similar way the *β*-acetyl thioacid chlorides **550** give the compounds **533** via the *β*-acetyldithio-*β*-chloro acid chlorides **551** [1122].



SCHEME 278

9.1.3. 3H-1,2-Dithiolium Salts

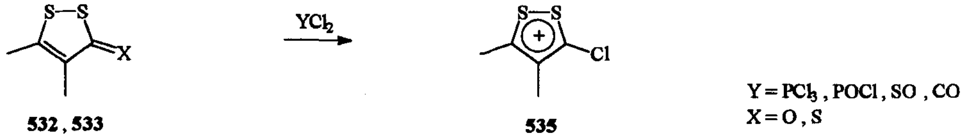
3*H*-1,2-Dithiolium salts **534** can be obtained in a manner similar to that for the 2*H*-1,3-dithiolium salts **35** by oxidation of the corresponding trithiones with peracetic acid [1123], hydrogen peroxide [1124], or nitric acid [1125]. Furthermore they are available from acyclic educts (e.g. **552** or **553**) by reaction with diacetyl disulfide in the presence of strong acids [1126].



SCHEME 279

9.1.4. *3-Chloro-1,2-dithiolium Salts*

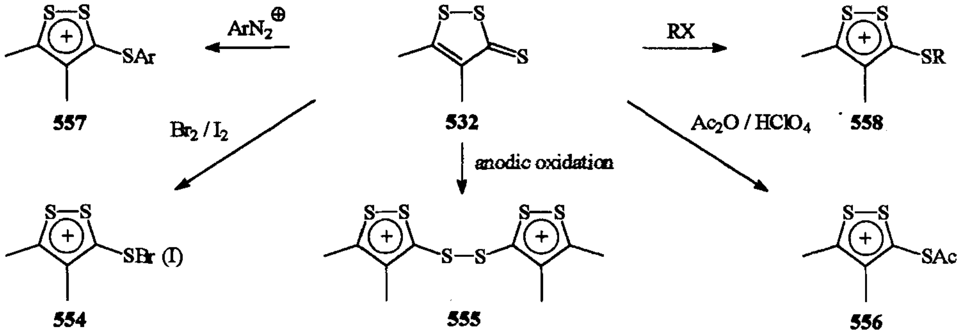
3-Chloro-1,2-dithiolium salts **535** can be synthesized from the corresponding 1,2-dithiole-3-thiones **532** or 1,2-dithiol-3-ones **533** by reaction with halogen transfer compounds (e.g. phosphorus pentachloride [1127], oxalyl chloride [1127,1128], phosphorus oxychloride [1127]).



SCHEME 280

9.1.5. *(Organylthio)-1,2-dithiolium Salts*

1,2-Dithiole-3-thiones **532** are compounds with a strongly polar thione group, which is readily be attacked by electrophiles. With halogens the sulfenyl halides **554** [1129] and by anodic oxidation the disulfides **555** [1130] are formed. In the presence of perchloric acid the acylation to the reactive acylthiodithiolium salts **556** is possible [1131]. Diazonium salts arylate to give the 3-(arylthio)-1,2-dithiolium salts **557** [1132]. Due to the simple replacement of the arylthio group by nucleophiles and due to their ready availability [1133] especially the 3-(alkylthio)-1,2-dithiolium salts **558** are of high preparative interest.



SCHEME 281

9.2. Unsuccessful Attempts to Synthesize 1,2-TTF

All attempts to make 1,2-TTF by deprotonation of the 3*H*-1,2-dithiolium salts **534** via the corresponding carbenes **559** failed. However, it has been claimed in a patent that methylthio, alkoxy and acetyloxy substituted 1,2-dithiolylium salts give rise to 1,2-TTF when treated with base in acetic anhydride [1134]. The deprotonation of the 3*H*-1,2-dithiolium salts **534** leads to product mixtures from which 1,2-dithiole-3-thiones **532** [1135,1136], thiathiophthenes **560** [1137], thieno[3,2-*b*]thiophenes **561** [1138] and a thieno[3,2-*c*]dithiin **562** [1134] could be isolated. The formation of these compounds can be explained via the 3-carbena-1,2-dithiole **559** as intermediate. Other reasons for the postulation of the carbene **559** as the primary deprotonation product of the dithiolium salt **534** are the results of the base catalysed H/D exchange [1135,1139] and the observation that the yields of trithiones **532** increase markedly if the deprotonation is carried out with additional amounts of sulfur [1135].

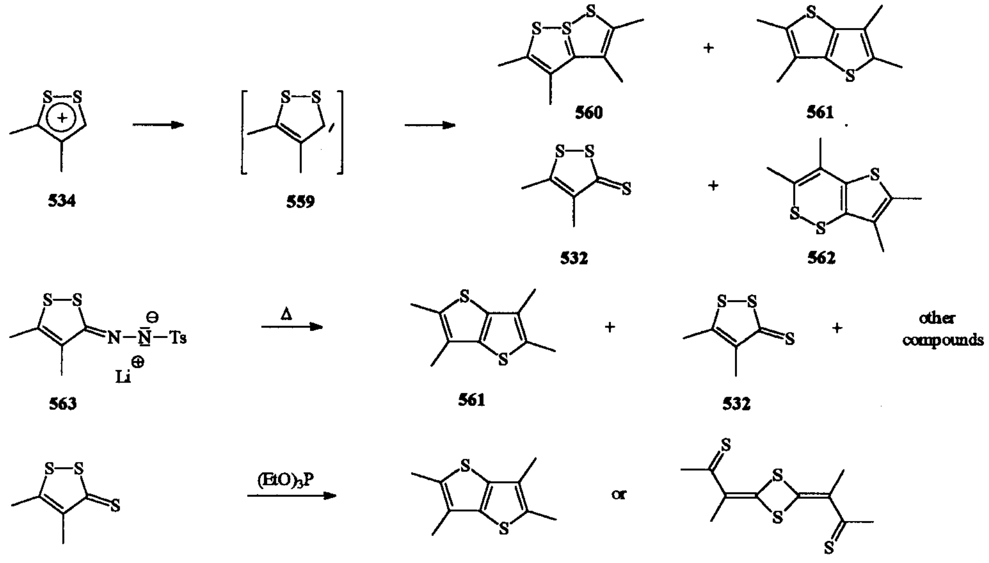
Also thermolysis of alkali salts of 1,2-dithiol-3-one hydrazones **563** leads not to 1,2-TTF, but to compounds of the types **532** and **561** [1136].

Furthermore, the reaction of trithiones **532** with trivalent phosphorus compounds—very successful in the synthesis of 1,3-TTF—leads to thieno[3,2-*b*]thiophenes **561** [1136,1140]. Alkylthio substituted trithiones **532** form with triethyl phosphite compounds, which have been ascribed erroneously the 1,2-TTF structure [1141]. It has, however, been shown that these products are actually the isomeric thioxodesaurines **564** [1142–1145]. The thioxodesaurines **564** could be formed via thioacyl thioketenes **565**, which are also intermediates by the pyrolysis of 1,2-dithiole-3-thiones **532** [1146].

The bis(ethylenedithio)-1,2-dithiol-3-one provides with trimethyl phosphite the corresponding thieno[3,2-*b*]thiophene **561** [1147].

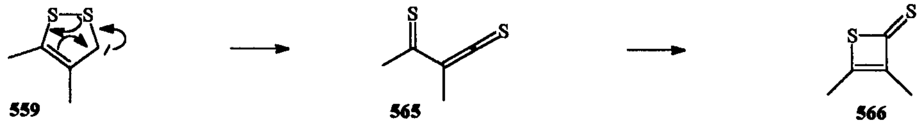
5-Phenyl-1,2-dithiole-3-thione reacts with triethyl phosphite in toluene at 70°C at pressures between 10 and 20 kbar and gives rise to complex mixtures. The parent 1,2-dithiole-3-thione provides with triphenylphosphine, tri-*n*-butylphosphine, trimethyl or triethyl phosphite a polymer (probably a polymer mixture) with a composition roughly that of $[C_3H_2S]_x$ and small amounts of phosphorous. The polymer is insoluble in all solvents, so that an identification of the structure cannot be given [1148].

In the case of the reaction of 5-(4-chlorophenyl)-4-cyano-1,2-dithiole-3-thione with trialkyl phosphites the formation of the corresponding 1,2-TTF is described [1149].



SCHEME 282

An explanation of the experimental observation that the postulated carbene **559** as intermediate does not yield 1,2-TTF has been given [1150]. These authors carried out quantum chemical calculations on a CNDO/2 basis. They came to the conclusion that the carbenes **559** isomerize very rapidly to the thiete-2-thiones **566** with S–S bond cleavage. The open-chain thioacyl thioketenes **565** are discussed as intermediates. According to this calculation the possible dimerization of the carbene **559** to the 1,2-TTF is kinetically depressed by competition reactions.

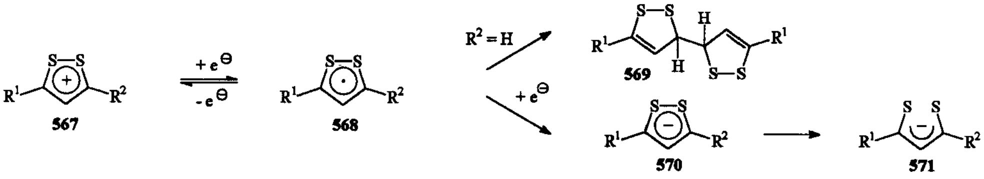


SCHEME 283

9.3. Synthesis of 1,2-TTF

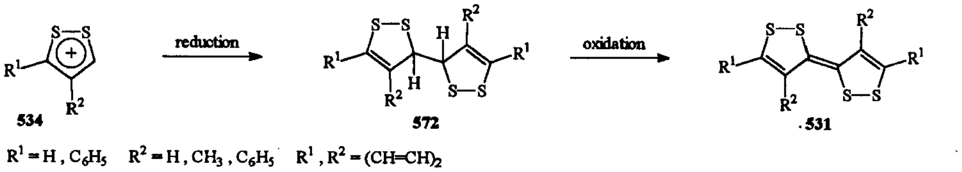
9.3.1. 1,2-TTF by Reductive Dimerization of 1,2-Dithiolium Salts

The cathodic reduction of the dithiolium salts **567** leads, with reception of one electron, to the corresponding 1,2-dithiolium radical **568**, which can dimerize to compound **569** [1151]. The stability of the radical **568** and the equilibrium **568**/**569** depend on the nature of the substituents R^1 and R^2 and the temperature. Whereas in the case of the radicals **568** with $R^2 = H$ the equilibrium lies definitely on the side of the dimers the equilibrium in the case of **568** with $R^1 = R^2 = Ph$ lies on the opposite side. Reception of a further electron leads to the dithiolium anions **570**. This reduction step is irreversible, the reason being the formation of the dithiodiketonate anion **571**. The intermediate steps **567**–**571** can also be carried out photochemically [1151].



SCHEME 284

Preferred reagents for preparative reductions for the synthesis of the dimers **572** are zinc and aqueous titanium(III) chloride solutions [1152]. Contrary to earlier claims [1153] some dimers **572** could be dehydrogenated by several oxidation agents to the 1,2-TTF **531** [1103,1152].

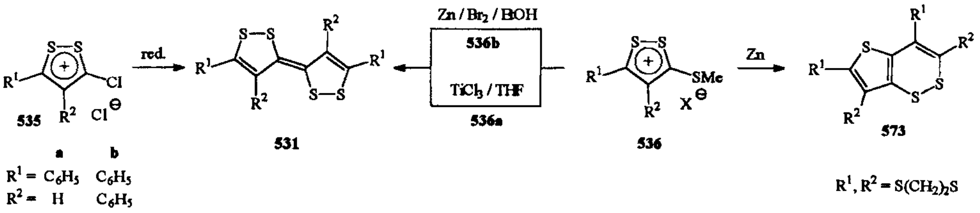


SCHEME 285

Reduction of 3-chloro-1,2-dithiolium salts **535** with zinc, silver, or aqueous titanium(III) chloride solution gives the 1,2-TTF **531** in one step [1152]. The yield in the reduction with activated zinc is increased by supersonication.

The conversion of the 3-methylthio-1,2-dithiolium salt **536b** to **531b** requires zinc as reducing agent and bromine as oxidative 'extractor' for the alkylthio groups. Zinc alone as reducing agent for the 4,5-bis(ethylenedithio)-3-methylthio-1,2-dithiolium iodide affords the corresponding thieno[3,2-*c*][1,2]dithiin **573** [1147].

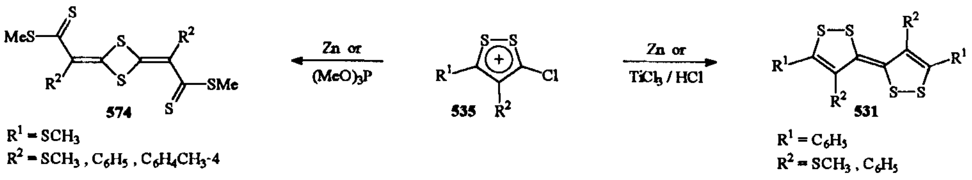
Reduction of the compound **536a** with titanium(III) chloride alone gave the 1,2-TTF **531a** in only about 3% yield.



SCHEME 286

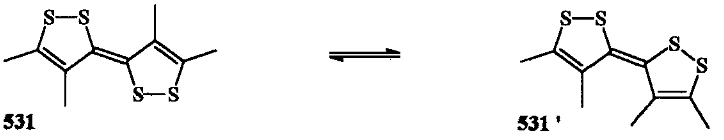
The dimerization of the 5-methylthio substituted 1,2-dithiolium salts with activated zinc or trimethyl phosphite gives the thioxodesaurines **574** [1143].

The choice of the reducing agent and the reduction conditions (solvent, temperature) have a great influence on the success of the dimerization reaction [1152].



SCHEME 287

Some 1,2-TTF **531** could be isolated in two isomeric forms, characterized by their different UV–Vis spectra. The conversion of one form into another—considered as the *cis–trans* isomers **531**/**531′**—can be carried out thermally or photochemically.

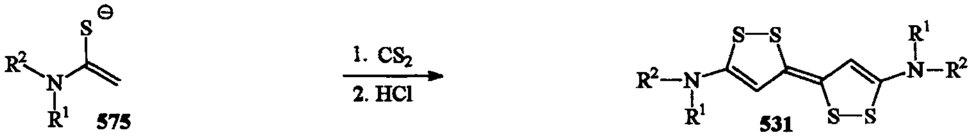


SCHEME 288

Besides the 1,2-TTF the reaction mixture also contains the corresponding trithiones **532**, in some cases additionally 1,2-dithiol-3-ones **533** and thieno[3,2-*b*]thiophenes **561**. The intermediate formation of the carbenes **559** has been discussed as one of the reasons for this observation.

9.3.2. Formation of 1,2-TTF in Other Ways

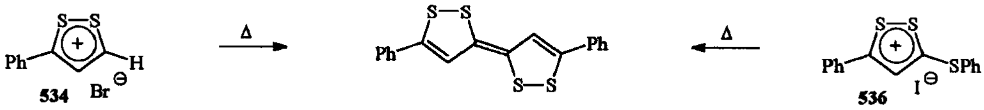
A further approach to 1,2-TTF starts from the thiolates **575**. Reaction of **575** with carbon disulfide, followed by treatment with hydrochloric acid, yields the amino substituted 1,2-TTF **531** in 7–30% yield [1154].



$R^1 = CH_3$ $R^2 = CH_3, C_6H_5$ $R^1, R^2 = (CH_2)_2, (CH_2)_2O(CH_2)_2$

SCHEME 289

Already before the first announcement of the preparation of 1,2-TTF the possible formation of 1,2-TTF by thermolysis of the salts **534** or **536** in the ion source of a mass spectrometer was reported [1155]. This was confirmed in a later publication [1156].

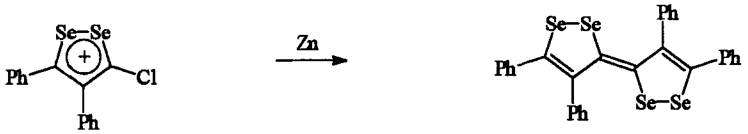


SCHEME 290

1,2-TTF and their data are summarized in Table XIII.

9.4. Synthesis of 1,2-TSF

Diphenyl substituted 1,2-tetraselenafulvalenes are obtained in low yield (5%) by reduction of the corresponding 1,2-diselenolium salts with activated zinc [1143].



SCHEME 291

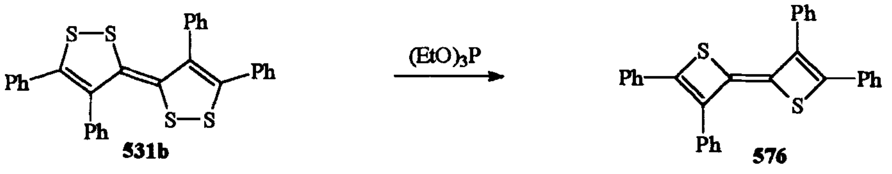
1,2-TSF and their data are summarized in Table XIV.

10. 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 it has only been reported that they are yellow. 1,2-TTF are thermally less stable than 1,3-TTF. In boiling tetraline compound

531b is converted into the thieno[3,2-*b*]thiophene **561** in about 80% yield [1103,1135]. Other 1,2-TTF react analogously. In some cases addition of sulfur during the thermolysis is a further reaction, so that the trithiones **532** and a thienodithiine **562** can be isolated.

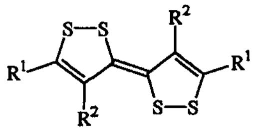
The reaction behaviour of 1,2-TTF with trivalent phosphorus compounds was studied in the case of **531b**. Whereas no reaction took place with triphenylphosphine in boiling benzene, with triethyl phosphite or tributyl phosphite a new compound was formed which contains two sulfur atoms less than **531b**. As a possible structure **576** was postulated.



SCHEME 292

In their redox properties the 1,2-TTF show great similarity to their 1,3-analogues. Depending on the nature and amount of the oxidizing agent, oxidation to the radical cation **577** or the dication **578** takes place. Neutral 1,2-TTF comproportionate with the dications **578** to the radical cations **577**. Zinc or titanium(III) chloride reduces

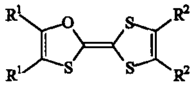
TABLE X Charge transfer complexes of 1,2-TTF with acceptors and their electrical conductivity (compressed powder)



R^1	*R*^{2}	*Acceptor*	σ_{RT} [S cm^{-1}]	*Reference*
Ph	H	DDQ[a]		1152
		TCNQ[b]	3-5	1157
Ph	Ph	DDQ	10^{-5}	1152, 1158
		TCNE[b]		1152
		TCNQ	10^{-5}	1158
		$TCNQF_4$	10^{-3}	1158
Ph	SMe	$TCNQF_4$	10^{-5}	1158
SMe	SMe	TCNQ	10^{-5}	1158
$(CH=CH)_2$	$(CH=CH)_2$	DDQ		1152
CH=CH-S	CH=CH-S	TCNQ	10^{-3}	1158

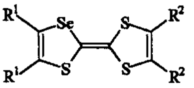
[a] both isomeric forms provide the same complex, [b] only one of the isomeric forms provides a complex, DDQ 2,3-dichloro-5,6-dicyanobenzoquinone, TCNE tetracyanoethylene, $TCNQF_4$ tetrafluorotetracyanoquinodimethane.

TABLE XI Molecular properties of monooxatrithiafulvalenes (redox potential in acetonitrile *vs.* sce)



R^1	R^2	Z	*m.p.* [°C] (*solvent*)	*Yield* [%]	λ_{max} (ε) [nm]	E_1^{Ox} [V]	E_2^{Ox}	*References*
$(CH{=}CH)_2$	$(CH{=}CH)_2$		154.7–156.9			0.72 0.1 M TBAT^k	1.22	306

TABLE XII Molecular properties of trithiamonoselenafulvalenes (redox potential in acetonitrile *vs.* sce)



R^1	R^2	Z	*m.p.* [°C] (*solvent*)	*Yield* [%]	λ_{max} (ε) [nm]	E_1^{Ox} [V]	E_2^{Ox}	*References*
$S(CH_2)_2S$	H	O, S $(EtO)_3P$	195	4.5	360 sh, 330 sh, 298, 218			1428
$S(CH_2)_2S$	$CH_2O(CH_2)_2Si(CH_3)_3$	O, S $(EtO)_3P$						1427
$S(CH_2)_2S$	$O(CH_2)_2O$	O $(EtO)_3P$	196	4.5	480, 313, 260 sh			1426
$S(CH_2)_2S$	$S(CH_2)_2S$		250					1427
$COOCH_3$	SCOS	O, S $(EtO)_3P$	204 dec.					586

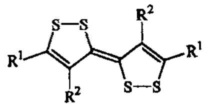
the salts **577** and **578** to the neutral 1,2-TTF. The 1,2-TTF are typical reversible redox systems [1135].

SCHEME 586

10.1. Charge-transfer Complexes of 1,2-TTF

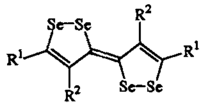
Like the analogous 1,3-TTF the 1,2-TTF also form charge-transfer complexes with several acceptors (Table X). Only 1 : 1 donor acceptor complexes have been isolated. In the electron spectra of the charge transfer complexes long-wavelength absorptions of the donor and acceptor radical ions have been identified. Although the first isolation of a charge transfer complex from a 1,2-TTF and TCNQ was reported in 1975 [1103], the experimental data available until now are very limited. General conclusions about the interdependence between structure and redox properties or electric conductivity of the donors **531** and their charge-transfer complexes cannot be drawn.

TABLE XIII Molecular properties of 1,2-tetrathiafulvalenes (redox potential in acetonitrile *vs.* sce)



R^1	*R^2*		*m.p.* [°C] (*solvent*)	*Yield* [%]	λ_{max} (ε) [nm]	E_1^{Ox} [V]	E_2^{Ox} [V]	*References*
CH_3	CH_3							1134
$N(CH_3)_2$	H		266 (DMF)	17				1154
$N(CH_2)_4$	H		263 (DMF)	30				1154
$O(CH_2)_4N$	H		268–269 (DMA)	7				1154
NC_6H_5 $\vert$ CH_3	H		265–266 ($CHCl_3/CCl_4$)	7				1154
SCH_3	SCH_3	*cis*	198 (CH_2Cl_2)	30	481, 440 sh, 350[k]			1141, 1223
		trans	238 (CH_2Cl_2)	45	473, 454 sh, 375[k]			1141
SCH_2S			181[i] (DMF/MeCN)	35	580, 540 sh, 390 sh, 370[a]			1141
$S(CH_2)_2S$			177[i]	38	580, 550 sh, 420 sh, 400[k]			1141
$COOCH_3$	SCH_3							1134
C_6H_5	H		179–180[L]	67				1103, 1152
			180–181[L]					1103, 1152
C_6H_5	CH_3		143–144 ($CHCl_3$)	59				1152
C_6H_5	SCH_3		208	16	550 (7950)[w]	0.30	0.52	1143
C_6H_4Cl-4	CN			20				1149
C_6H_5	C_6H_5		228.5 (CH_2Cl_2)	49	526[u] 502[d] 502[E] 497[w]			1103, 1152
			290	52	500 (12 600)[w]	0.21	0.43	1143
$(CH{=}CH)_2$			147–149[L] (CH_2Cl_2/MeOH)	41				1152
			212–213[L] (CH_2Cl_2/MeOH)					1152

TABLE XIV Molecular properties of 1,2-tetraselenafulvalenes (redox potential in acetonitrile *vs.* sce)



*R*¹	*R*²	*m.p* [°*C*] (*solvent*)	*Yield* [%]	λ_{max} (*ε*) [nm]	E_1^{Ox} [V]	E_2^{Ox}	*References*
C_6H_5	C_6H_5	304	5	497 (15 800), 338 (63 000)[w]			1143

[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, [j]70% perchloric acid, [k]in dichloromethane, [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 dioxane, [u]in carbon disulfide, [v]in 1,1,2-trichloroethane, [w]in chloroform, [x]in propionitrile, [y]in butyronitrile, [z]*vs.* normal hydrogen electrode, [A]in 1,2-dichlorobenzene, [B]in KBr, [C]in dichloromethane/acetonitrile, [D]*vs.* ferrocene, [E]in carbon tetrachloride, [F]in 1,1,2-trichloroethane at 90°C, [G]in 1,1,2-trichloroethane at 70°C, [H]in 1,2-dichloroethane at 50°C, [I]in dimethyl sulfoxide, [K]in hexamethylphosphoric triamide, [L]one isomer, [M]in benzonitrile at 60°C, [N]*vs.* Ag wire, [O]benzonitrile/carbon disulphide (1 : 1), [P]*vs.* Ag/Ag* (0.1 M), [Q]in toluene, [R]in dichloromethane/acetonitrile (3 : 1), [S]*vs.* glassy carbon electrode, [T]in 1,2,4-trichlorobenzene, [U]in 1,1,2,2-tetrachloroethane at 40°C, [V]in toluene/acetonitrile (4 : 1) at – 45°C, [W]in acetonitrile/chloroform (5 : 1), [X]in dichloromethane/acetonitrile (2 : 1), [Y]in toluene/acetonitrile (4 : 1), [Z]in 1,1,1-trichloroethane, [α] in nitrobenzene, [β] in acetone.

TBAA: tetrabutylammonium hexafluoroarsenate, TBAHP: tetrabutylammonium hexafluorophosphate, TBAP: tetrabutylamonium perchlorate, TBAT: tetrabutylammonium tetrafluoroborate, TEAP: tetraethylammonium perchlorate, TEAT: tetraethylammonium tetrafluoroborate, TEAB: tetraethylammonium bromide, TPAT: tetrapropylammonium tetrafluoroborate.

*peak potential, potential in parantheses indicate an irreversible redox reaction.

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