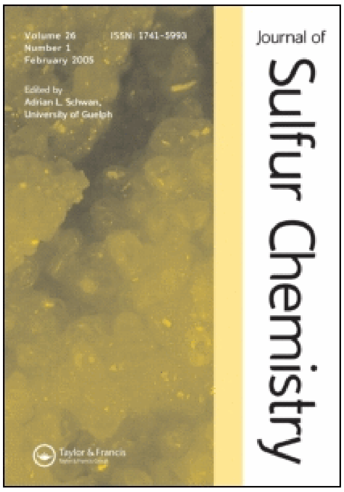

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Synthesis, Reactions, and Selected Physico-Chemical Properties of 1,3- and 1,2-Tetrachalcogenafulvalenes

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

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(Received September 28, 1992)

In continuation of a 1987 review in this journal this review describes additional syntheses of 1,3- and 1,2-tetrachalcogenafulvalenes, the chemical transformation of substituents, and the synthesis of polymers with 1,3-tetrathiafulvalene units in the backbone and in the side chain. For some charge-transfer complexes with tetrachalcogenafulvalenes as donor superconducting properties are reported.

Selected properties (melting points, UV/VIS absorption data, and oxidation potentials) of 1,2- and 1,3-tetrachalcogenafulvalenes, prepared after publication of our 1987 review, are summarized in appropriate tables.

Key words: Tetrachalcogenafulvalenes, synthesis, TTF, polymeric TTF.

INTRODUCTION

Since the publication of our 1987 review concerning synthesis, reactions, and selected properties of 1,3- and 1,2-tetrachalcogenafulvalenes,[1] many new tetrachalcogenafulvalenes have been synthesized by the reviewed and by modified methods. 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 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.

These relations between structures of donors and properties of conducting CT complexes are, inter alia, at the focus of international conferences,[2-9] reviews,[10,11] and books.[12,13] In this review a survey of additional methods for the preparation of tetrachalcogenafulvalenes and their properties since our 1987 review is given.

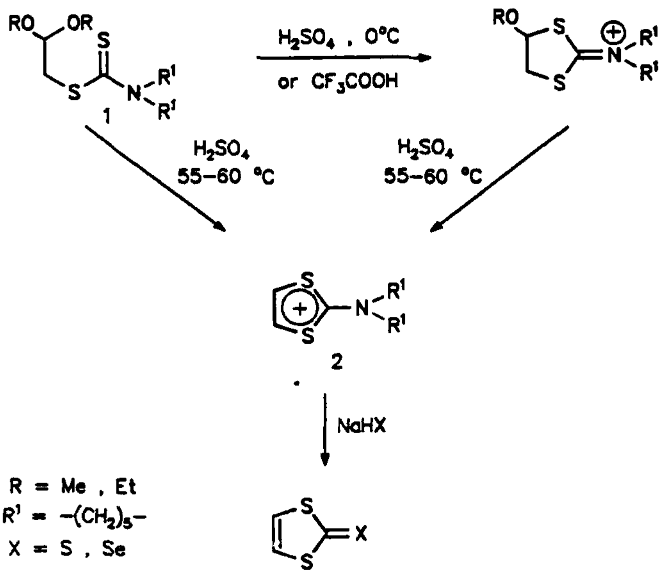
1. SYNTHESIS of TETRATHIAFULVALENES (TTF)

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

Cyclization of β-keto *N*,*N*-dialkyldithiocarbamates 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 **1**.[14] In the acetalized form cyclization in sulfuric acid at 55–60 °C affords the 2-(*N*,*N*-dialkylamino)-1,3-dithiolium salts **2**, which can be converted to 1,3-dithiole-2-thiones or 1,3-dithiole-2-selones 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.

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 Chapter 6.1.).

An alternative synthesis of selenium substituted TTF starts from the air and moisture stable organometallic complex bis(tetrabutylammonium) bis(2-thioxo-1,3-dithiole-4,5-diselenolato) nickelate (II) **3**.[15–17] This complex is formed by lithiation of 1,3-dithiole-2-thione, followed by treatment with powdered selenium, nickel chloride and tetrabutylammonium bromide.

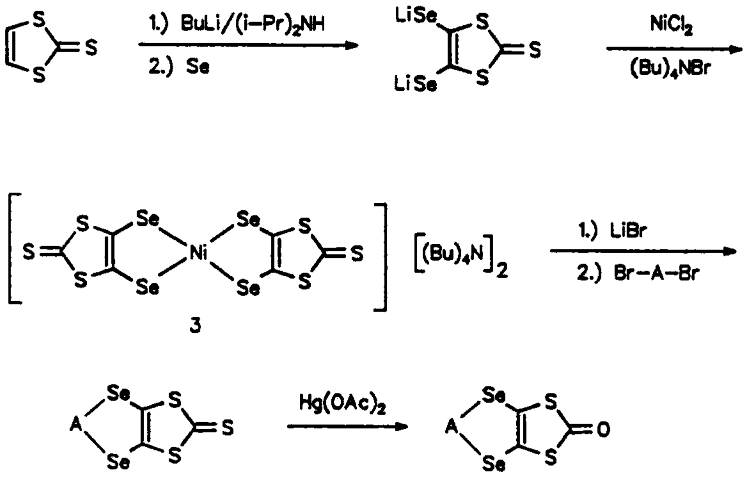
Upon reflux of the nickel complex **3** with lithium bromide and dibromoalkanes the corresponding alkylenediseleno-1,3-dithiole-2-thiones are formed, which can be converted to alkylenediseleno-1,3-dithiol-2-ones with mercuric acetate in a refluxing mixture of chloroform and acetic acid.

Also vinylenedithio-1,3-dithiole-2-thione has been lithiated and substituted in this way, the selenium insertion being facilitated by supersonic waves.[18]

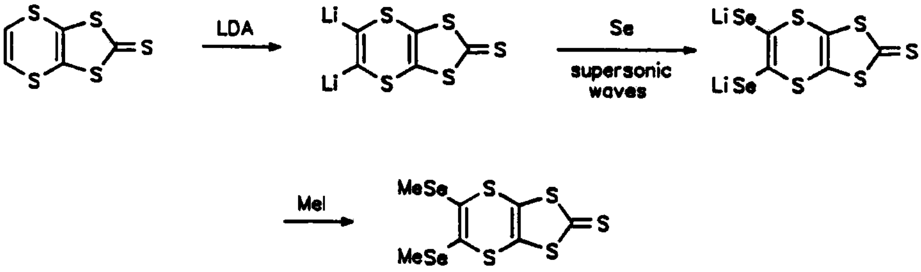
Dialkyl substitued vinylenedithio-1,3-dithiole-2-thiones have been prepared by refluxing the complex bis(tetraethylammonium) bis-(2-thioxo-1,3-dithiole-4,5-dithiolato) zincate(II) **4** with propargyl halides in acetone and subsequent isomerization with *p*-toluenesulfonic acid.[19]

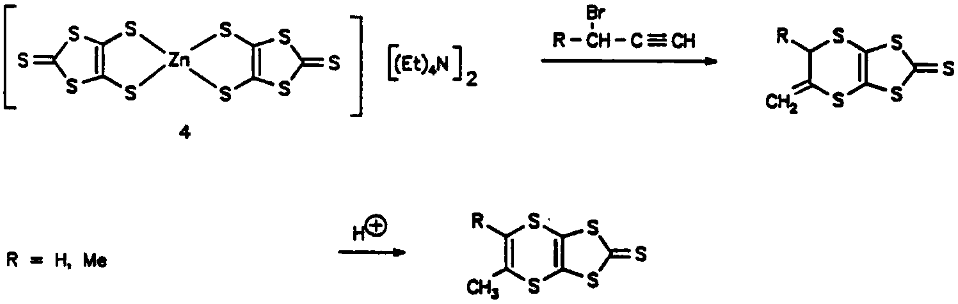
This reaction is assumed to be analogous to the formation of dimethylene-tetrahydro-TTF **9** by cleavage of 4,5-bis(propargylthio)-1,3-dithiol-2-ones in alkaline solution (see Chapter 1.2.).[20]

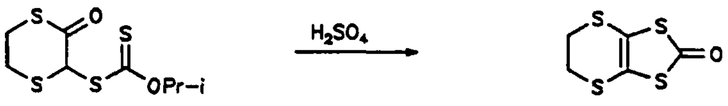
1,3-Dithiol-2-ones can be prepared directly by cyclization of β-keto *O*-alkyl dithiocarbonates with concentrated sulfuric acid. 4,5-Ethylenedithio-1,3-dithiol-2-one has been synthesized in 50% yield by treatment of 2-oxo-3-(*i*-propoxythiocarbonylthio)-1,4-dithiane **5** with sulfuric acid at 0 °C.[21–22]



A = $-CH_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$







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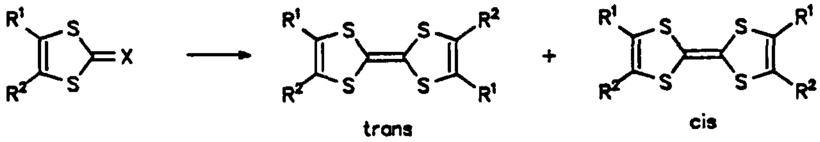
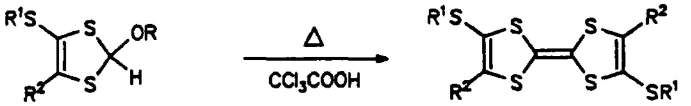
1.2. *The Formation of cis and trans Isomers of TTF*

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



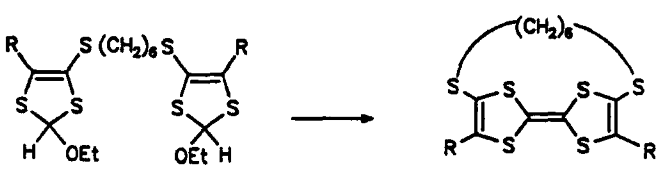
Only in the case of thermolysis of 2-alkoxy-1,3-dithioles in the presence of trichloroacetic acid in refluxing benzene the formation of trans isomers could be demonstrated by X-ray analysis.[23]

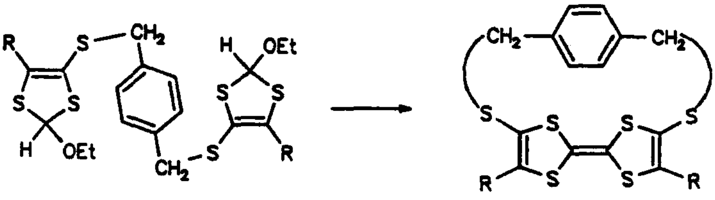


In two cases, however, bridged 2-alkoxy-1,3-dithioles form the cis isomers in nearly quantitative yield.[24]

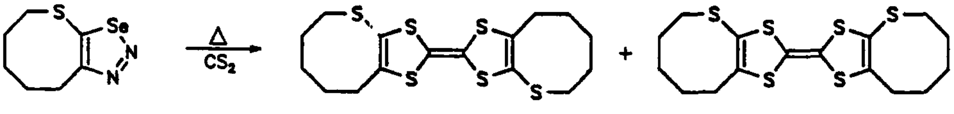
Mostly the properties of cis and trans isomers of TTF are very similar and prevent a distinction or separation. In a ^{1}H NMR study for the first time evidence of an acid catalysed trans-cis isomerization in the case of bis(4-[*p*-chlorophenyl]-5-methylthio)-TTF was obtained.[25] The cis-trans equilibrium was too rapidly established to permit isolation of the pure cis form. Only the trans isomer could be recovered after concentration of the solution. 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 **6** in carbon disulfide could be proved.[26]

In some cases the cis/trans mixture could be separated. The diacetalized tetraformyl-TTF, prepared by desulfurizing coupling of the corresponding thione with dicobalt octacarbonyl, is obtained as a mixture of essentially equal amounts of the cis and trans isomer.[26a] 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





R = p-MeC$_6$H$_4$



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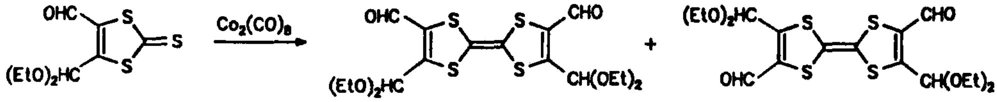
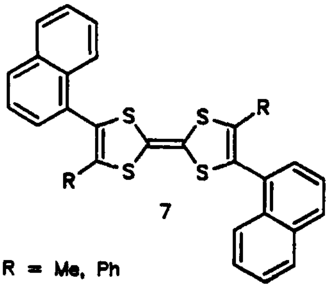


influence of acids on the cis isomer. This is in contrast to the above bis(4-[*p*-chlorophenyl]-5-methylthio)-TTF.

Bulky substituents modify the properties of cis and trans isomers so much that a separation can be carried out based on different solubilities in the case of α-naphthylmethyl-**7**[27] or α-naphthylphenyl-**7**, ß-naphthylphenyl substituted and dihydrophenanthreno annelated TTF **8**.[28]



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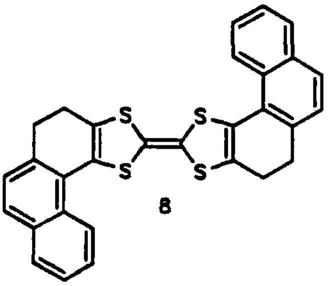
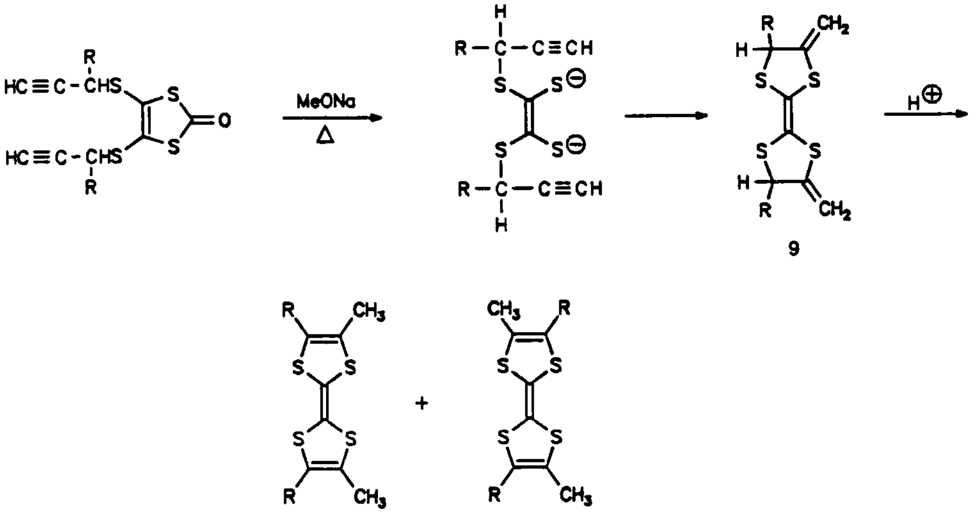
R = Me, Ph



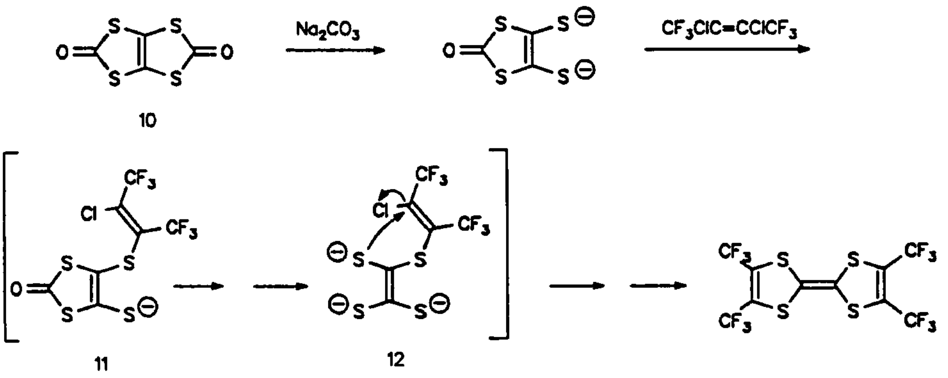
8

In an alternative synthesis by stereospecific cyclization of 4,5-bis(propargylthio)-1,3-dithiol-2-one due to the cis relationship of the sulfide groups in the intermediate the cis isomer should be formed. However, the resulting dimethylene-tetrahydro-TTF **9** are oils, making X-ray analysis unfeasible. After isomerization

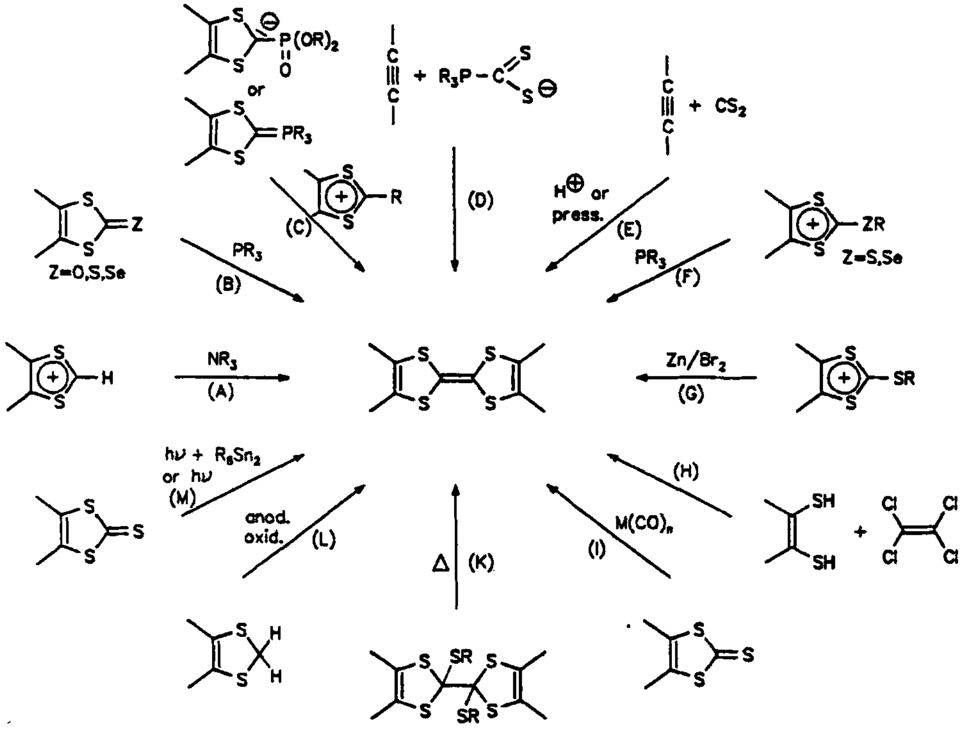


with *p*-toluenesulfonic acid in refluxing benzene a mixture of cis and trans isomers is formed, as an X-ray structure determination proves.[20] This cis-trans mixture is probably formed by protonation of the central double bond, followed by isomerization.

In a nucleophilic substitution reaction tetrakis(trifluoromethyl)-TTF is formed by alkaline hydrolysis of 1,3,4,6-tetrathiapentalene-2,6-dione **10** in the presence of 2,3-dichlorohexafluoro-2-butene under phase transfer conditions.[22,29] It is proposed that the intermediate **11** is formed after initial attack of the alkyl halide

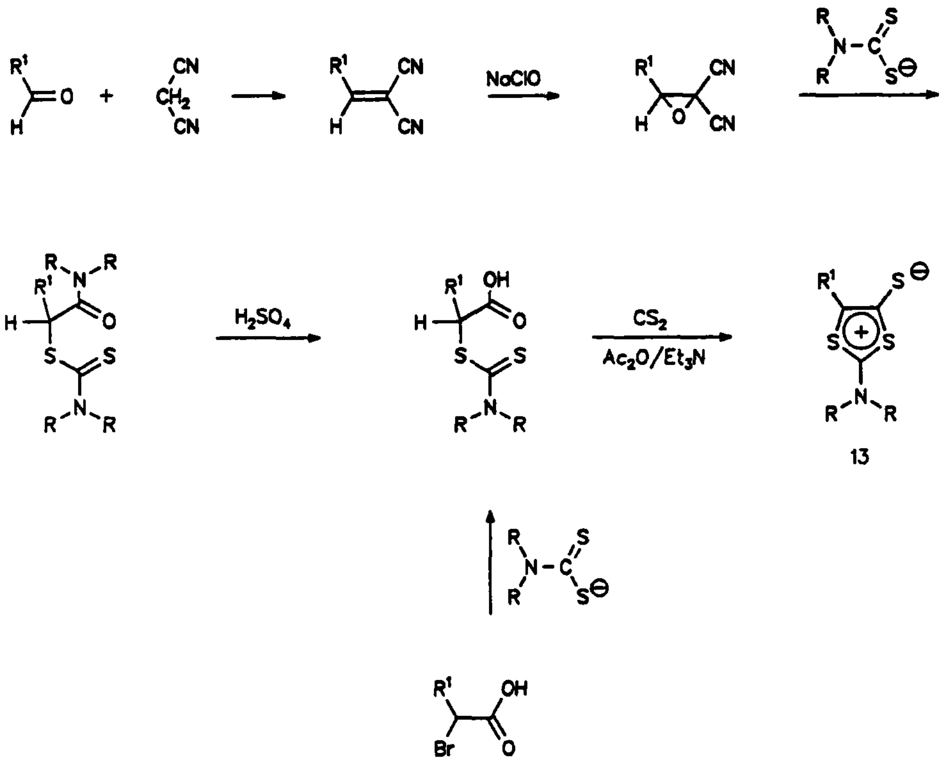


by the dianion. The extremely electron-withdrawing substituent could facilitate the opening of the second ring and stabilize the resulting trianion **12**. After intramolecular cyclization and reaction with a second mole of alkyl halide the tetrakis(trifluoromethyl)TTF would be formed. Further methods for the synthesis of TTF are summarized in Scheme 1 and discussed in the next chapters as far as there are new aspects.



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

In a known way TTF are formed by deprotonation of 2*H*-1,3-dithiolium salts with tertiary aliphatic amines.[1] Intermediate for 2*H*-1,3-dithiolium salts are the mesoionic 1,3-dithioles **13** which can be obtained in a multi-step reaction.[30,31] An improved synthesis of **13** involves reaction of 2-halo carboxylic acid with excess *N*,*N*-dialkyldithiocarbamate in ethanol.The crude product is treated (without further purification) with acetic acid anhydride and triethylamine, followed by reaction with excess carbon disulfide.[32]

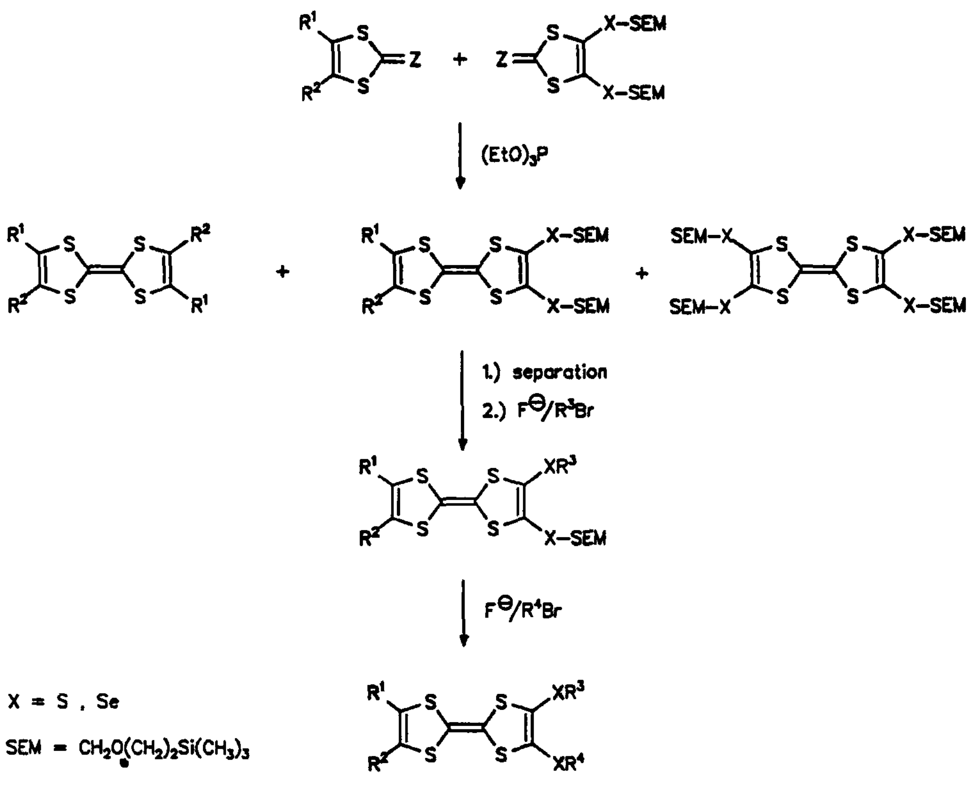


After alkylation of **13** the 2*H*-1,3-dithiolium salts can be obtained via the known route, i.e. by reduction with sodium borohydride and subsequent deamination with strong acid.

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

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 compounds thus formed can easily be 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 alkyl bromides.[33]

The yield of alkylthio substituted TTF by coupling of 1,3-dithiole-2-thiones with trimethyl or triethyl phosphite is increased under high pressure (400–800 MPa).[34]



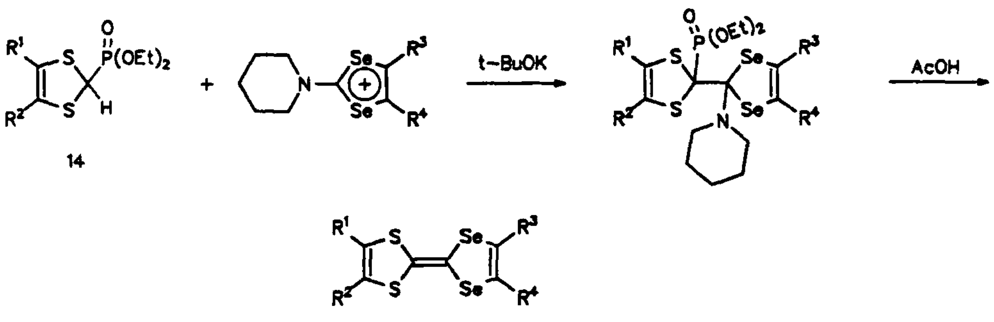
1.5. *Treatment of 1,3-Dithiolium Salts with Phosphoranes or Phosphonates (Method C)*

Unsymmetrical TTF derivatives can be prepared by reaction of 1,3-dithiol-2-ylidenephosphoranes with 1,3-dithiolium salts in the presence of triethylamine. The instability of the 1,3-dithiol-2-ylidenephosphoranes under the reaction conditions leads to the formation of variable amounts of symmetrical TTF. Therefore, purification of the mixture by column chromatography is necessary.[35]

This side reaction and the formation of symmetrical TTF can be avoided by coupling of phosphonate esters of various substituted 1,3-dithioles **14** with 2-amino-1,3-dithiolium salts under Wittig-like conditions. Yields of pure, unsymmetrical TTF are typically 30–50%.[36]

1.6. *Miscellaneous Methods*

A pyrrolo-annelated 1,3-dithiole-2-thione has been converted to the corresponding TTF by irradiation in benzene in the presence of hexabutyldistannane in 15–



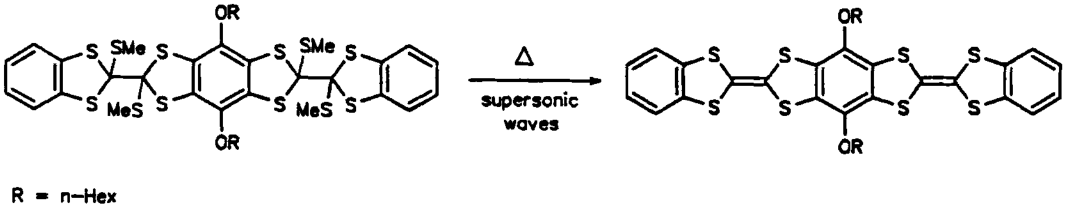
14

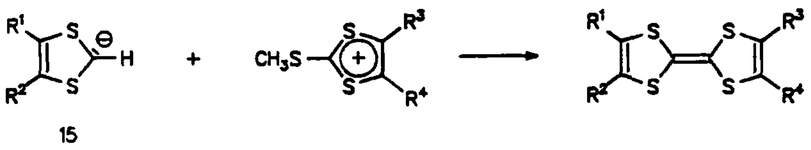
20% yield (method M).[37] Thermolysis of orthothiooxalates to TTF is accelerated by catalytic amounts of *p*-toluenesulfonic acid. Addition of catalytic amounts of *p*-toluenesulfonic acid does not influence the thermolysis of bis(orthothiooxalates) in 1,1,2,2-tetrachloroethane at 130 °C.[38,39]

However, upon supersonic irradiation the reaction proceeds at lower temperatures (70 °C) with a yield as high as 80%.[40,41] A coupling method leading to unsymmetrical TTF involves treatment of 1,3-dithiole anions **15** with electrophilic 1,3-dithiolium salts.

In addition to the expected condensation products, symmetrical TTF, derived from **15**, probably via carbenes, are formed.[42]

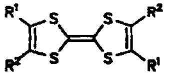
TTF and their data are summarized in Table 3.





15

TABLE 3
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

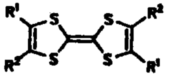


R^1	R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
H	H					0,38 0,1 M TBAHP	0,77	135
						0,35 0,1 M TBAP	0,71	136
						0,40 0,1 M TBAHP[k)]	0,82	79
						0,38 0,1 M TBAP[q)]	0,74	102
n-C_6H_{13}	H	A	oil	25				137
n-$C_{18}H_{37}$	H	A	33	65				137
CH_3	CH_3					0,29 0,1 M TBAP	0,65	136
n-C_5H_{11}	n-C_5H_{11}	A	48-49 (pentane)					137

$-CH_2-O-CH_2-$				92		0,35 0,1 M TBAHP[q]	0,66	91
$-CH_2-S-CH_2-$		B Z=S $(MeO)_3P$	222-230	40	530 (215), 463 (360), 365 (2 040), 308 (12 850)[v]	0,55 0,1 M TBAHP[q]	0,72	138
$-CH_2-SO_2-CH_2-$		B Z=Se $(MeO)_3P$	222 dec.	47		0,65 0,1 M TBAHP[q]	0,80	138, 139
$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CO-$		B Z=Se Ph_3P	270-278 dec. (DMF)	50	444 (3 800), 318 (13 800), 305 (14 100)[l]	0,7	1,0	140
CH_2OH	CH_2OH		220 dec.	80		0,39 0,1 M TBAP[q]	0,65	26a, 52
				39				91
$-S-(CH_2)_5-$ $-(CH_2)_5-S-$			127-129	26				26
H	$C_{18}H_{37}S$		62	12				141
C_2H_5	CH_3S		86 (MeCN)	69		0,43 0,1 M TBAP	0,71	30, 136, 142
$CH_3(CH_2)_{10}$	$HOOC(CH_2)_{10}S$		119 (MeCN)	60				31

(Continued)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)



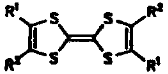
R^1	R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
$CH_3(CH_2)_{10}$	CH_3OOCCH_2S		58 (MeCN)	78				31
$CH_3(CH_2)_{10}$	$HOOCCH_2S$		90-95 (MeCN)	88				31
p-$HOOCC_6H_4$	$CH_3(CH_2)_{17}S$		153 (EtOAc)	90				31
p-ClC_6H_4	$HOOC(CH_2)_{10}S$		139 (MeCN)	66				31
p-ClC_6H_4	$(C_6H_5)_2CHS$		218 (EtOH)	98				31
p-$CH_3C_6H_4$	$(C_6H_5)_2CHS$		222 (EtOH)	92				31
$CH_3(CH_2)_{10}$	$(C_6H_5)_2CHS$		86 (EtOH)	93				31
$CH_3(CH_2)_8$	$Br(CH_2)_3S$			91				31

$CH_3(CH_2)_{10}$	$Br(CH_2)_3S$		99	31
$p\text{-}ClC_6H_4$	$Br(CH_2)_3S$		90	31
$p\text{-}CH_3C_6H_4$	$Br(CH_2)_3S$		86	31
$CH_3(CH_2)_{10}$	$Br(CH_2)_4S$		97	31
$CH_3(CH_2)_{10}$	$Br(CH_2)_6S$	58 (EtOAc)	95	31
$p\text{-}ClC_6H_4$	$Br(CH_2)_6S$		87	31
$p\text{-}CH_3C_6H_4$	$Br(CH_2)_6S$		89	31
$p\text{-}ClC_6H_4$	$N_3(CH_2)_3S$		87	31
$CH_3(CH_2)_{10}$	$N_3(CH_2)_6S$		85	31
$p\text{-}ClC_6H_4$	$N_3(CH_2)_6S$		86	31
$p\text{-}CH_3C_6H_4$	$N_3(CH_2)_6S$		87	31
$p\text{-}ClC_6H_4$	$(CH_3O)_2OPNH(CH_2)_3S$			31
$p\text{-}CH_3C_6H_4$	$(CH_3O)_2OPNH(CH_2)_3S$			31
$CH_3(CH_2)_{10}$	$(CH_3O)_2OPNH(CH_2)_6S$			31
$p\text{-}ClC_6H_4$	$(CH_3O)_2OPNH(CH_2)_6S$			31

(*Continued*)

TABLE 3 (*Continued*)

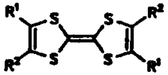
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

 R^1	R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
p-ClC_6H_4	$H_2N(CH_2)_3S$							31
p-$CH_3C_6H_4$	$H_2N(CH_2)_3S$							31
$CH_3(CH_2)_{10}$	$H_2N(CH_2)_6S$							31
p-ClC_6H_4	$H_2N(CH_2)_6S$							31
p-ClC_6H_4	C_4H_9SnS							31
p-$CH_3C_6H_4$	C_4H_9SnS							31
$CH_3(CH_2)_{10}$	C_4H_9SnS							31
$COOCH_3$	CH_3S					0,63 0,1 M TBAP	0,93	136, 142
CH_3S	CH_3S		96,5			0,55		143
			95-96			0,64 0,1 M TBAP[a)]	0,93	144

						0,40 0,1 M TBAP	0,73	136
						0,50 h,k)	0,81	145
$(CH_3)_3Si(CH_2)_2OCH_2S$	$(CH_3)_3Si(CH_2)_2OCH_2S$	B Z=O,S $(EtO)_3P$	64-65		470, 380, 328, 305, 278, 254, 225$^{a)}$			33
CH_3OOCCH_2S	CH_3OOCCH_2S		108 (THF)	18	390, 326, 307, 264, 210$^{a)}$			146
p-$CH_3COOC_6H_4CH_2S$	p-$CH_3COOC_6H_4CH_2S$	B Z=O Z=S $(EtO)_3P$		 71 27				98a
C_2H_5S	C_2H_5S		72-73			0,64 0,1 M TBAT$^{n)}$	0,94	144
						0,52 0,1 M TBAT	0,77	105
$ClCH_2CH_2S$	$ClCH_2CH_2S$	B Z=O Z=S $(EtO)_3P$	158-160 (MeCN)	 89 76	386, 330, 310$^{t)}$	0,61 0,1 M TBAT	0,87	88, 105
$BrCH_2CH_2S$	$BrCH_2CH_2S$	B Z=O $(EtO)_3P$	169-171 (CCl_4/ benzene)	90	388, 330, 310$^{t)}$	0,62 0,1 M TBAT	0,88	105

(Continued)

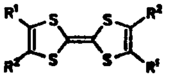
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

 R^1	R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
ICH_2CH_2S	ICH_2CH_2S		166-167 (benzene)	78	389, 332, 308$^{t)}$	0,60 0,1 M TBAT	0,87	105
$NCCH_2CH_2S$	$NCCH_2CH_2S$							147
$HOCH_2CH_2S$	$HOCH_2CH_2S$		137-138 (acetone)	95	379, 330, 310$^{t)}$	0,53 0,1 M TBAT	0,74	105
$CH_3SCH_2CH_2S$	$CH_3SCH_2CH_2S$	B Z=O $(EtO)_3P$	65-67 (ether/acetone) 5:1	73		0.60	0,84	106
$C_6H_5COOCH_2CH_2S$	$C_6H_5COOCH_2CH_2S$	B Z=O $(EtO)_3P$	107-109 (i-PrOH)	96	388, 330, 308$^{t)}$	0,59 0,1 M TBAT	0,91	105
$p\text{-}ClC_6H_4SO_2OCH_2CH_2S$	$p\text{-}ClC_6H_4SO_2OCH_2CH_2S$		146-148 (benzene)	94	385, 330, 308$^{t)}$	0,60 0,1 M TBAT	0,87	105
$CH_2{=}CHS$	$CH_2{=}CHS$		45-46		475, 388, 325 sh, 309, 299 sh, 229$^{a)}$	0,59 0,1 M TBAHP$^{q,k)}$	0,92	33, 88

C_3H_7S	C_3H_7S		96			143
		30-31		0,63 0,1 M TBAT[n]	0,94	144
C_4H_9S	C_4H_9S	24,6	87			143
		26-26,5		0,64 0,1 M TBAT[n]	0,94	144
$C_5H_{11}S$	$C_5H_{11}S$	31,5-32,5		0,64 0,1 M TBAT[n]	0,93	144
$C_6H_{13}S$	$C_6H_{13}S$	29,5-30,5		0,64 0,1 M TBAT[n]	0,93	144
$C_7H_{15}S$	$C_7H_{15}S$	44-46		0,64 0,1 M TBAT[n]	0,94	144
$C_8H_{17}S$	$C_8H_{17}S$	48,5-49,5		0,64 0,1 M TBAT[n]	0,94	144
$C_9H_{19}S$	$C_9H_{19}S$	57,5-59		0,64 0,1 M TBAT[n]	0,94	144
$C_{10}H_{21}S$	$C_{10}H_{21}S$	59-60		0,64 0,1 M TBAT[n]	0,94	144
$C_{11}H_{23}S$	$C_{11}H_{23}S$	64-65,5		0,64 0,1 M TBAT[n]	0,94	144

(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

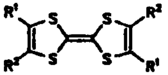
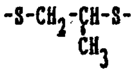
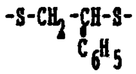
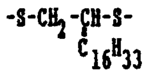
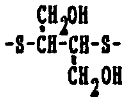
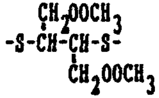


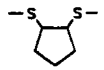
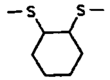
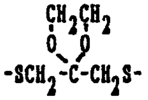
R^1	R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} (ε) [nm]	E_1^{Ox} [V]	E_2^{Ox}	references
$C_{12}H_{25}S$	$C_{12}H_{25}S$		68-69			0,64 0,1 M TBAT$^{n)}$	0,95	144
$C_{13}H_{27}S$	$C_{13}H_{27}S$		74,5-75,5			0,64 0,1 M TBAT$^{n)}$	0,95	144
$C_{14}H_{29}S$	$C_{14}H_{29}S$		78-79			0,64 0,1 M TBAT$^{n)}$	0,94	144
$C_{15}H_{31}S$	$C_{15}H_{31}S$		80-81,5			0,64 0,1 M TBAT$^{n)}$	0,94	144
$C_{16}H_{33}S$	$C_{16}H_{33}S$		81,5-83			0,65 0,1 M TBAT$^{n)}$	0,94	144
$C_{17}H_{35}S$	$C_{17}H_{35}S$		84-85,5			0,64 0,1 M TBAT$^{n)}$	0,94	144
$C_{18}H_{37}S$	$C_{18}H_{37}S$		92			0,64 0,1 M TBAT$^{n)}$	0,94	144
			87,7					143

C_6H_5S	C_6H_5S		167-169 (EtOAc/hexane)	64		0,55 0,1 M TBAHP$^{k)}$	0,90	97
$-S-\overset{COOCH_3}{CH}-S-$		B Z=O $(EtO)_3P$	198	17	346, 306, 220$^{a)}$			148
$-O-(CH_2)_2-O-$		B Z=Se $(MeO)_3P$	178	63	517 (148), 337 (9 690), 315 (11 400), 200 (13 300)$^{a)}$	0,44 0,1 M TBAHP$^{g)}$	0,70	149, 150
$-S-(CH_2)_2-S-$					480 (290), 345 sh (10 000), 320 (17 000), 197 (36 000)$^{a)}$	0,57 0,1 M TBAHP$^{g)}$	0,83	149, 150
						0,56 0,1 M TBAP	0,80	136
						0,54 0,1 M TBAHP$^{n)}$	0,96	135
						0,49 0,1 M TBAHP$^{k)}$	0,64	151
						0,69 0,1 M TBAP$^{c)}$	0,82	18
$-S-(CD_2)_2-S-$		B Z=O $(EtO)_3P$	244 dec.	74	481 (269)$^{c)}$			152

(*Continued*)

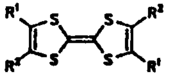
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

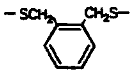
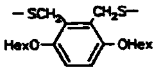
 R^1 R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
	Z=S $(EtO)_3P$		23	470 (288), 348 (12 600), 322 (14 800)$^{w)}$			152
 $-S-CH_2-\underset{CH_3}{CH}-S-$	B Z=S $(EtO)_3P$	175	35	345, 321, 260$^{k)}$			153
 $-S-CH_2-\underset{C_6H_5}{CH}-S-$	B Z=S $(EtO)_3P$	207-210 dec.	50	344 (39 800), 308 (56 300), 218 (170 000)$^{d)}$	0,47 0,1 M TBAHP$^{k)}$	0,62	151
 $-S-CH_2-\underset{C_{16}H_{33}}{CH}-S-$	B Z=S $(EtO)_3P$	109-110 (hexane)	10	218 (170 000)$^{d)}$	0,1 M TBAHP$^{k)}$		154
 $-S-\overset{CH_2OH}{CH}-\underset{CH_2OH}{CH}-S-$		165-167 (MeCN)	80	500 (450), 345 (10 000), 323 (18 000)$^{p)}$	0,62$^{e,g)}$	0,87	155
 $-S-\overset{CH_2OOCH_3}{CH}-\underset{CH_2OOCH_3}{CH}-S-$	B Z=O $(EtO)_3P$	138-140 (MeCN)	59	333 (12 200), 319 (16 600)$^{t)}$	0,65$^{e,g)}$	0,80	155

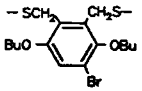
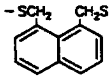
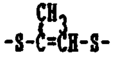
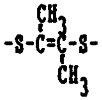
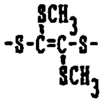
					0,62 0,1 M TBAP	0,90	136
					0,61 0,1 M TBAP	0,87	136
	B Z=O $(EtO)_3P$		66				156
$-SCH_2-CO-CH_2S-$	K	235-236 (pyridine)	51				157
		> 340			0,68 0,1 M TBAHP[g,v)]	1,04	156
$-SCH_2-O-CH_2S-$	B Z=O Z=S $(EtO)_3P$	260-262 (pyridine)	 5 18	500 (400), 396 (5 130), 335 (13 200)[t)]	0,67 0,1 M TBAP	0,90	136, 142, 158, 159
	K		65				157
$-SCH_2-S-CH_2S-$	A	275-278	90				157
$-S-(CH_2)_4-S-$	B Z=S $(EtO)_3P$	151 (CH_2Cl_2/ MeOH)	37	310, 227[k)]	0,53 0,1 M TBAHP[g,k)]	0,95	160, 161
					0,67 0,1 M TBAP	1,01	136

(Continued)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

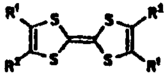
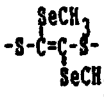
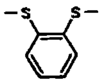
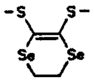
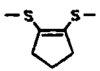
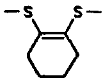
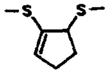


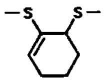
R^1 R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
$-S(CH_2CH_2O)_2CH_2CH_2S-$							162
$-S(CH_2CH_2O)_3CH_2CH_2S-$	B Z=S $(EtO)_3P$	211-212 (MeCN)	44		0,52	$0{,}75^{h,k)}$	145, 162
$-SCH_2-CH=CH-CH_2S-$	B Z=Se $(MeO)_3P$	165-167 dec.	43	408 (955), 333 (8 700), 301 (12 300)$^{t)}$			163
	B Z=S $(MeO)_3P$	270 dec. (pyridine)	50	408 (1 290), 380 (5 000), 340 (12 300), 275 (10 960)$^{v)}$			164
	B Z=O Z=S $(EtO)_3P$	265-267 dec. $(CHCl_3)$	 18 61	340, 286, 243, 231$^{k)}$	0,52 0,1 M TBAHP$^{g,k)}$	0,98	161
	B Z=S $(EtO)_3P$	184	33	417 (2 239), 333 (15 813) 314 (16 143), 227 (27 855)$^{k)}$	0,33 TBAHP$^{k)}$	0,82	166, 167

	B Z=S (EtO)$_3$P	206 dec.	50	303 (22 730)$^{k)}$	0,39 TBAHP$^{k)}$	0,84	165, 167
	B Z=O Z=S (EtO)$_3$P	243-244 dec. (CH$_2$Cl$_2$)	 26 11	334, 294, 237, 220, 204$^{k)}$	0,53 0,1 M TBAHP$^{g,k)}$	1,06	160, 161
-S-CH=CH-S-	B Z=O (EtO)$_3$P	> 220 (pyridine)	43	480 (355), 340 (14 450) 313 (14 120)	0,68 0,1 M TBAP$^{e)}$	0,94	136, 168, 169
	Z=O (EtO)$_3$P	227-230 (CHCl$_3$)	72	340 (6 910), 316 (6 750)$^{c)}$	0,83 0,1 M TBAP$^{c)}$		170, 171
 $-S-\overset{CH_3}{C}=CH-S-$	B Z=O (EtO)$_3$P	204 dec. (CHCl$_3$)	92	342 (4 900), 316 (4 900)$^{c)}$	0,80 0,1 M TBAP$^{c)}$		170, 171
 $-S-\overset{CH_3}{C}=\underset{CH_3}{C}-S-$	B Z=O (EtO)$_3$P	249-250 (CHCl$_3$)	97	344 (3 310), 314 (3 160)$^{c)}$	0,80 0,1 M TBAP$^{c)}$		19, 170
	B Z=O (EtO)$_3$P	> 230 dec. (pyridine)	75	490 (426), 344 (14 120), 312 (13 200)	0,65 0,1 M TBAP$^{e)}$	0,91	136, 168, 169
 $-S-\overset{SCH_3}{C}=\underset{SCH_3}{C}-S-$	B Z=O (EtO)$_3$P	200 dec. (CCl$_4$)	68	337 (20 000), 308 (21 400)$^{c)}$	0,83 0,1 M TBAP$^{c)}$		172

(Continued)

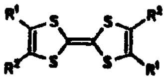
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

 R^1 R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V] E_2^{Ox}	references
 $-S-\underset{SeCH_3}{\overset{SeCH_3}{C=C}}-S-$	B Z=O $(EtO)_3P$	185 dec. (CCl_4)	75	338 (20 000), 306 (23 430)$^{c)}$	0,86 0,1 M TBAP$^{c)}$	18
	B Z=O $(EtO)_3P$	287 dec. (CCl_4)	75	495, 347, 303$^{g)}$	0,75* 1,13* 0,1 M TBAHP$^{k)}$	22
	B Z=S $(EtO)_3P$	> 320	13	340 sh, 312, 274$^{k)}$		173
	B Z=O $(EtO)_3P$	238-239 dec. (pyridine)	64	490 (645), 348 (27 300) 313 (33 100)$^{f)}$	0,76 1,02 0,1 M TBAP$^{e)}$	136, 169
	B Z=O $(EtO)_3P$	270 dec. (pyridine)	57	490 (708), 345 (29 350), 316 (44 600)$^{f)}$	0,69 0,97 0,1 M TBAP$^{e)}$	136, 169
	B Z=O $(EtO)_3P$	228-229 dec. (pyridine)	40	488 (416), 348 (14 100), 320 (13 800)$^{f)}$	0,67 0,96 0,1 M TBAP$^{e)}$	136, 169

		B Z=O $(EtO)_3P$	250 dec. (pyridine)	47	480 (416), 347 (15 100), 321 (19 100)$^{t)}$	0,61 0,1 M TBAP$^{e)}$	0,91	136, 169
C_6H_5COS	C_6H_5COS	G	163-169	1		0,66 0,1 M TBAP	0,89	136, 142, 174
		I $M=Co_2$ n=8	195	25		0,66 0,1 M TBAHP$^{k)}$	0,87	175
CH_3Se	CH_3Se		93,5-93,7 (hexane/benzene)	52		0,58 0,1 M TBAT$^{n)}$	0,93	95
			88-89 (EtOAc/hexane)	80		0,54	0,93	97
C_2H_5Se	C_2H_5Se		62,7-63,5 (hexane/benzene)	70				95
			57-58 (ether/hexane)	45				92
C_3H_7Se	C_3H_7Se		37,4-38,3 (hexane/benzene)	63				95
				85		0,44 0,1 M TBAHP$^{k)}$	0,86	97
C_4H_9Se	C_4H_9Se		38,8-39,3 (hexane)	55				95
				84		0,44 0,1 M TBAHP$^{k)}$	0,86	97

(*Continued*)

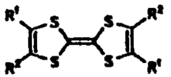
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

 R^1	R^2	preparative method*	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
$C_5H_{11}Se$	$C_5H_{11}Se$		29,9-30,7 (hexane)	56				95
				90		0,51 0,1 M TBAHP$^{k)}$	0,92	97
$C_6H_{13}Se$	$C_6H_{13}Se$		32,5-32,9 (hexane)	56				95
$C_7H_{15}Se$	$C_7H_{15}Se$		39,0-39,7 (hexane)	62				95
$C_8H_{17}Se$	$C_8H_{17}Se$		48,7-49,2 (hexane/benzene)	69				95
$C_9H_{19}Se$	$C_9H_{19}Se$		56,0-56,8 (hexane/benzene)	65				95
$C_{10}H_{21}Se$	$C_{10}H_{21}Se$		62,2-62,8 (hexane/benzene)	84				95
$C_{11}H_{23}Se$	$C_{11}H_{23}Se$		66,2-67,5 (hexane)	65				95

$C_{12}H_{25}Se$	$C_{12}H_{25}Se$		74,3-75,2 (hexane)	70				95
$C_{13}H_{27}Se$	$C_{13}H_{27}Se$		79,7-80,3 (hexane)	78				95
$C_{14}H_{29}Se$	$C_{14}H_{29}Se$		83,3-84,1 (hexane)	73				95
$C_{15}H_{31}Se$	$C_{15}H_{31}Se$		86,0-86,6 (hexane)	78				95
$C_{16}H_{33}Se$	$C_{16}H_{33}Se$		87,7-89,2 (hexane)	75				95
$C_{17}H_{35}Se$	$C_{17}H_{35}Se$		90,4-91,3 (hexane)	71				95
$C_{18}H_{37}Se$	$C_{18}H_{37}Se$		94,2-94,6 (hexane)	77				95
$-Se-CH_2-Se-$			192-195 (CS_2)	31		0,11 0,1 M TBAT$^{e,h)}$	0,36	92, 93
		B Z=O $(EtO)_3P$	257 dec. (dichloro-benzene)	69	326 (12 200)$^{A)}$	0,40 0,1 M TBAA$^{e)}$	0,67	15
$-Se-(CH_2)_2-Se-$			220-223 (CS_2)	35		0,15 0,1 M TBAT$^{e,h)}$	0,55	92, 93

(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

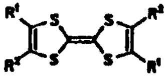


R^1	R^2	preparative method˙	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V] E_2^{Ox}	references
		B Z=O $(EtO)_3P$	241 (CS_2)	60	345 (15 800)$^{m)}$	0,44 0,77 0,1 M TBAA$^{e)}$	15, 16
-Se-$(CH_2)_3$-Se-		B Z=O $(EtO)_3P$	272-277 (dichloro-benzene)	55	400 (6 000), 340 (16 000)	0,45 0,77 0,1 M TBAA$^{e)}$	15, 17
				65			93
C_6H_5Se	H		114				83
C_6H_5Se	C_6H_5Se		154-156 (THF/hexane)	75		0,50 0,89 0,1 M TBAHP$^{k)}$	97
			116				83
CH_3Te	CH_3Te		175-176	66		0,52 0,91 0,1 M TBAT$^{n)}$	94
C_2H_5Te	C_2H_5Te		90,2-91,2	67		0,51 0,91 0,1 M TBAT$^{n)}$	94

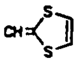
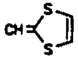
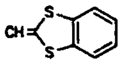
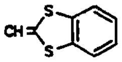
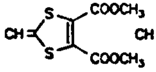
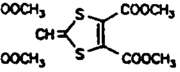
		86-87 (ether/hexane)	32			92
C_3H_7Te	C_3H_7Te	62,2-62,7	60	0,51 0,1 M TBAT$^{n)}$	0,91	94
C_4H_9Te	C_4H_9Te	85,7-86,5	38	0,51 0,1 M TBAT$^{n)}$	0,91	94
$C_5H_{11}Te$	$C_5H_{11}Te$	56,9-57,4	62	0,51 0,1 M TBAT$^{n)}$	0,93	94
$C_6H_{13}Te$	$C_6H_{13}Te$	46,0	68	0,52 0,1 M TBAT$^{n)}$	0,92	94
$C_7H_{15}Te$	$C_7H_{15}Te$	49,9-50,2	67	0,51 0,1 M TBAT$^{n)}$	0,92	94
$C_8H_{17}Te$	$C_8H_{17}Te$	57,7	48	0,51 0,1 M TBAT$^{n)}$	0,92	94
$C_9H_{19}Te$	$C_9H_{19}Te$	65,2-65,7	63	0,51 0,1 M TBAT$^{n)}$	0,92	94
$C_{10}H_{21}Te$	$C_{10}H_{21}Te$	72,7	52	0,52 0,1 M TBAT$^{n)}$	0,93	94
$C_{11}H_{23}Te$	$C_{11}H_{23}Te$	77,5-78,5	58	0,52 0,1 M TBAT$^{n)}$	0,93	94
$C_{12}H_{25}Te$	$C_{12}H_{25}Te$	82,2-82,7	58	0,52 0,1 M TBAT$^{n)}$	0,92	94

(Continued)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

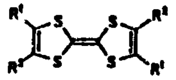


R^1	R^2	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
$C_{13}H_{27}Te$	$C_{13}H_{27}Te$		87,2-87,4	33		0,50 0,1 M TBAT[n]	0,91	94
$C_{14}H_{29}Te$	$C_{14}H_{29}Te$		89,2-90,3	45		0,50 0,1 M TBAT[n]	0,90	94
$C_{15}H_{31}Te$	$C_{15}H_{31}Te$		92,2-93,0	52		0,50 0,1 M TBAT[n]	0,90	94
$C_{16}H_{33}Te$	$C_{16}H_{33}Te$		94,2-94,6	77		0,51 0,1 M TBAT[n]	0,91	94
$C_{17}H_{35}Te$	$C_{17}H_{35}Te$		96,2-97,2	69		0,51 0,1 M TBAT[n]	0,91	94
$C_{18}H_{37}Te$	$C_{18}H_{37}Te$		97,5-98,2	76		0,51 0,1 M TBAT[n]	0,91	94
$COOC_4H_9$	H					0,65 0,1 M TBAP	0,98	136, 142
CF_3	CF_3		89,5-90,5 sublim.	40		1,23 0,1 M TBAHP[k]	1,45	29

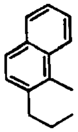
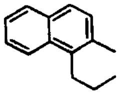
CHO	CH(OC$_2$H$_5$)$_2$	I M=Co$_2$ n=8	172 130-132	70	526 (4 800)$^{k)}$ 504 (4 250)$^{k)}$	trans isomer cis isomer	0,95* 0,1 M TBAP$^{m)}$	1,30*	26a
							0,84* 0,1 M TBAP$^{v)}$	1,24*	53, 103
CH(OC$_2$H$_5$)$_2$	CH(OC$_2$H$_5$)$_2$	B Z=S (MeO)$_3$P	136,5-137,5	42			0,62* 0,1 M TBAP$^{m)}$	1,05*	26a
(CH$_3$)$_2$C=CH	(CH$_3$)$_2$C=CH		114-115 (ether/EtOH)	60			0,33* 0,1 M TBAP	0,65*	26a
C$_2$H$_5$OOCCH=CH	C$_2$H$_5$OOCCH=CH		250	92			0,86* 0,1 M TBAP	1,14*	26a
CH$_3$COCH=CH	CH$_3$COCH=CH		> 260	91			0,78* 0,1 M TBAP	0,95*	26a
C$_6$H$_5$CH=CH	C$_6$H$_5$CH=CH		152-154 (THF)	73			0,42* 0,1 M TBAP	0,67*	26a
				70			0,19 0,1 M TBAP$^{q)}$	0,34	102
				73					102
				65			0,34 0,1 M TBAP$^{v)}$	0,65	102
I	H		91-92		478 (398), 372 sh (2 570), 314 (12 900), 288 (12 900)		0,58 0,1 M TBAP	0,96	101, 136

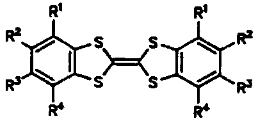
(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)



R^1	R^2		preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
							0,63 0,1 M TBAP[g]	1,01	101
Cl	Cl			221-223	15		0,83 0,1 M TBAH[k]	1,12	90
					30				86
Br	Br			227-228	15		0,79 0,1 M TBAH[k]	1,13	90
α-naphthyl	H		A	79-81	87	395 sh (2 420), 292 (32 000)[w]	0,32 0,1 M LiCl[f]	0,67	27
β-naphthyl	H		A	243-247	92	416 (6 640), 323 (33 500)[w]	0,32 0,1 M LiCl[f]	0,67	27
α-naphthyl	CH_3	cis	A	110-111	43	482 sh (360), 395 (2 170), 296 (35 000)[w]	0,30 0,1 M LiCl[f]	0,66	27
α-naphthyl	CH_3	trans	A	206-209	43	482 sh (415), 395 (2 560), 296 (38 500)[w]	0,30 0,1 M LiCl[f]	0,66	27

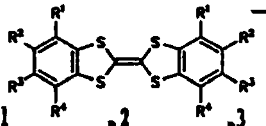
β-naphthyl	CH_3			A	216-218	90	585 sh (420), 391 (5 500), 330 (20 500) w)	0,30 0,1 M LiCl f)	0,66	27
			cis	A	204-208	20	436 (5 840), 328 (22 000) A) 423 (5 790), 328 (30 000) n)	0,32 0,05 M TEAP A)	0,69	28
			trans	A	224-228	63	446 (8 570), 328 (31 500) A) 433 (8 240), 328 (30 000) n)	0,31 0,05 M TEAP A)	0,70	28
				A	> 360 (1,2-dichloro-benzene)	80	430 (7 260), 365 sh, 334 (80 910) A)	0,37 0,05 M TEAP A)	0,76	28



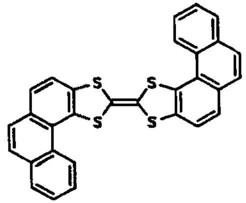
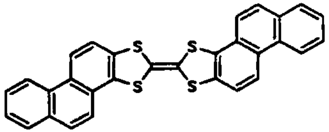
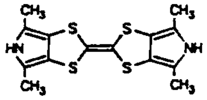
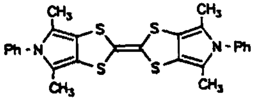
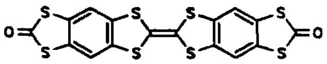
R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} (ε) [nm]	E^{Ox}_1 [V]	E^{Ox}_2	references
H	CH_3S	CH_3S	H	B Z=O $(EtO)_3P$	281,5-282,5 (xylene)	45		0,43 0,1 M TBAHP k)	1,04	176
CH_3S	CH_3S	CH_3S	CH_3S	B Z=S $(EtO)_3P$	302-304	90	409 (10 500) w)	0,74 0,1 M TBAP n)	1,09	107, 177

(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

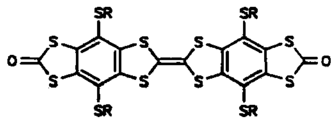
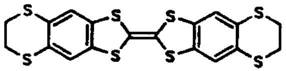
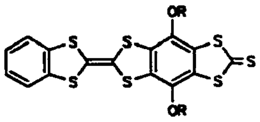
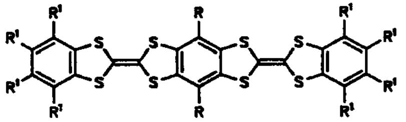


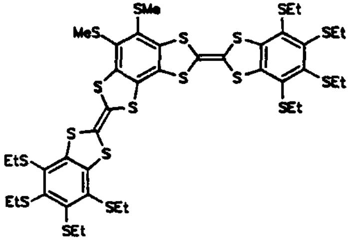
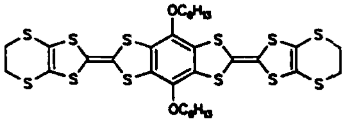
R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
C_2H_5S	C_2H_5S	C_2H_5S	C_2H_5S	B Z=S $(EtO)_3P$	161-163	62	409 (11 250)$^{W)}$	0,71 0,05 M TBAP$^{B)}$	1,09	177
$C_5H_{11}S$	$C_5H_{11}S$	$C_5H_{11}S$	$C_5H_{11}S$	B Z=S $(EtO)_3P$	155-157	40	410 (12 050)$^{W)}$	0,74 0,05 M TBAP$^{B)}$	1,11	177
$-S(CH_2)_2S-$		$-S(CH_2)_2S-$		B Z=S $(EtO)_3P$	> 360	35	381 (6 170)$^{A)}$	0,90 0,05 M TBAP$^{A)}$		177
-S-CO-S-		-S-CO-S-		B Z=O $(EtO)_3P$	> 360	89	368 sh$^{A)}$			177
CH_3S	$-SCH_2S-$		CH_3S		> 360	73	416$^{W)}$			107

	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V] E_2^{Ox}	references
	B Z=S $(EtO)_3P$	359-361 (1,2-dichlorobenzene)	63	396 (11 860), 335 (24 855)$^{A)}$	0,53 0,95 0,05 M TEAP$^{A)}$	28
	B Z=S $(EtO)_3P$	> 360	61	387 (6 210), 328 (36 000)$^{A)}$	0,52 0,98 0,05 M TEAP$^{A)}$	28
	M R=n-Bu	> 300			0,31 0,70 0,1 M TBAHP	178
	M R=n-Bu				0,39 0,74 0,1 M TBAHP	178
	B Z=O $(EtO)_3P$	> 320 (1,2,4-trichlorobenzene)	96			176

(Continued)

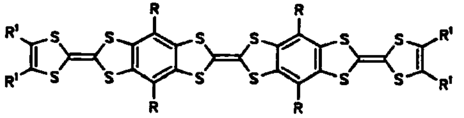
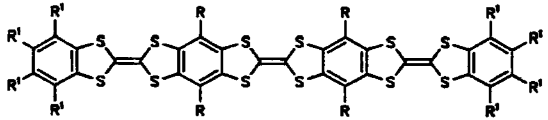
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

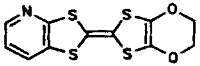
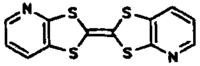
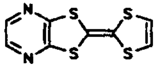
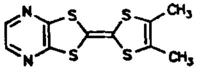
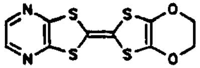
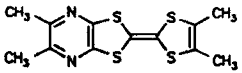
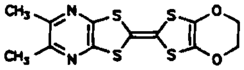
		preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
		B Z=O $(EtO)_3P$						
	R: Me		> 360	96	413, 303, 263$^{w)}$			107
	R: Pent		343-345	86	413 (12 600), 303 (39 800), 264 (56 250)$^{w)}$	0,90 0,01 M TBAP$^{n)}$	1,20	107
		B Z=O $(EtO)_3P$	> 320 (1,2-dichlorobenzene)	73		0,45 0,1 M TBAHP$^{k)}$		176
	R: Et	K	273	82				179
	R: Hex	K		87				39
	R: Di-t.but.-benzyl	K						180
	R R^1 O-Et H		280 dec.					38

O-Hex	H	K	198-199 ($CHCl_3$)	82	313 (60 000), 276 (51 500), 247 (36 000) k)			38, 179
O-Di-t.butyl-benzyl	H	K	242 dec.	68	314 (56 100), 277 (46 000), 247 (41 300) k)	0,46 1,13 0,1 M TBAHP k)	0,68 1,29	38, 41, 179, 180
S-iso-Amyl	H	K		66		0,44 1,10 TBAHP k)	0,68 1,29	41
S-iso-Amyl	S-Me	K						41
S-iso-Amyl	S-Et	K				0,41 1,06 TBAHP k)	0,63 1,22	41
						0,54 1,06 TBAHP k)	0,69 1,22	41
		K		86		0,38 0,95 TBAHP k)	0,59 (1,16)	40
		B Z=S $(EtO)_3P$		2,5				

(*Continued*)

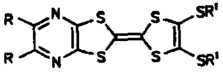
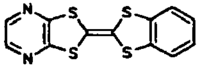
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

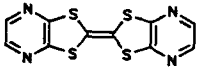
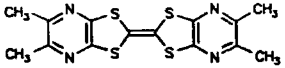
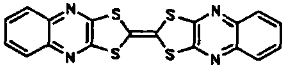
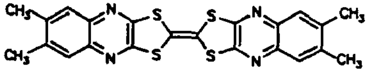
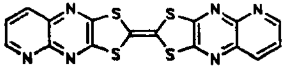
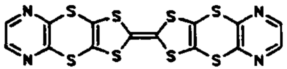
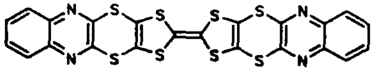
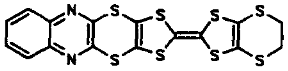
		preparative method*	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V] E_2^{Ox}	references
							
R	R^1						
S-iso-Amyl	S-Hex	B Z=S (EtO)$_3$P	320	58	442, 322, 266$^{k)}$	0,34 0,44 0,69 0,78 1,10 1,33 TBAHP$^{G)}$	181
							
R	R^1						
O-Et	H	B Z=S (EtO)$_3$P		16			179
O-Hex	H	B Z=S (EtO)$_3$P		28			39

	S-iso-Amyl	S-Et	B Z=S $(EtO)_3P$	> 360	91	431 (34 670)$^{f)}$, 318 (112 200), 265 (93 300)$^{k)}$	0,44 0,61 0,81 1,01 1,28 TBAHP$^{p)}$	181
			B Z=O,S $(EtO)_3P$	206	5,6			182
			B Z=S $(EtO)_3P$	278 ($CHCl_3$)	25	358 (2 290), 302 (3 420), 280 (3 420), 211 (8 700)		183
			B $(EtO)_3P$	184		420$^{a)}$		184
			B $(EtO)_3P$	249		420$^{a)}$	0,63 1,02 0,1 M TEAP	184
			B Z=O $(EtO)_3P$	209	6	430, 294 - 311 sh, 240$^{a)}$		108
			B $(EtO)_3P$	290		414$^{a)}$		184
			B Z=O $(EtO)_3P$	> 280	4	402, 290 - 311 sh, 238 sh, 218sh$^{a)}$		108

(*Continued*)

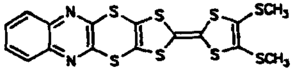
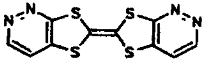
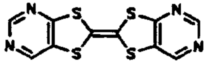
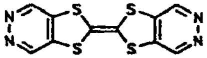
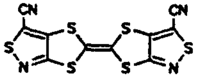
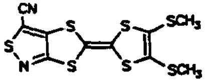
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

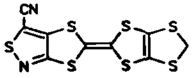
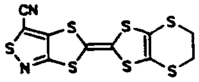
		preparative method*	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
		B Z=S $(EtO)_3P$						185
R	R^1							
H	CH_3		169	7				185
H	$-CH_2-$		218	6	$404^{a)}$	0,68	1,07	184, 185
H	$-(CH_2)_2-$		209	5	414, 326 sh, $306^{a)}$	0,68	1,02	185, 186
						0,1 M TBAP		184
H	$-(CH_2)_3-$		222	9				185
H	$-CH-CH_2-$ CH_3		145	6				185
CH_3	CH_3		195	9				185
CH_3	$-CH_2-$		208	5				185
CH_3	$-(CH_2)_2-$		243	5	$398^{a)}$	0,69	1,05	184, 185
CH_3	$-(CH_2)_3-$		261	6				185
CH_3	$-CH-CH_2-$ CH_3		187	5				185
$-(CH=CH)_2-$	$-(CH_2)_2-$		272	7				185
		B $(EtO)_3P$	242		$408^{a)}$			184

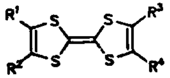
	B Z=S (EtO)$_3$P	303	35	395, 300 sh, 277$^{a)}$	0,89 0,1 M TEAP	1,17	185, 187, 188
					(1,05*) 0,1 M TBAP$^{q)}$		26a
	B Z=S (EtO)$_3$P	> 310	22		0,99 0,1 M TEAP	1,28	185, 187
	B Z=S (EtO)$_3$P	> 310	32	445, 300 sh, 265$^{k)}$			185, 188
	B Z=S (EtO)$_3$P	> 310	27				185
	B Z=S (EtO)$_3$P	> 310	19				185
		295	65				185
	B Z=S (EtO)$_3$P	350-351 dec. (1,2,4-trichlorobenzene)	69				189
	B Z=S (EtO)$_3$P	252-255		307$^{p)}$	0,82 0,1 M TBAT$^{v)}$	1,06	189

(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
	B Z=S $(EtO)_3P$	179-181		445 (2 240), 337 (12 300), 307 (12 900), 247 (21 900)$^{p)}$	0,78 0,1 M TBAT$^{v)}$	1,27	189
 cis/trans mixture	B Z=S $(EtO)_3P$						188
 cis/trans mixture	B Z=S $(EtO)_3P$						188
	B Z=S $(EtO)_3P$	300 dec.					53, 188
	B Z=O $(EtO)_3P$	> 300	52	400			190
	B Z=O,S $(EtO)_3P$	136	3	430			190

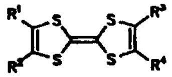
				B Z=O,S $(EtO)_3P$	234	6	430		190
				B Z=O,S $(EtO)_3P$	247	10	434		190



R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
H	H	$-(CH_2)_4-$			122			0,42 0,1 M TBAP$^{v)}$	0,84	191
$-(CH_2)_3-$		$-(CH_2)_4-$			217			0,34 0,1 M TBAP$^{v)}$	0,83	191
CH_3	CH_3	CH_3	CH_3S		119 (hexane)	51		0,28 0,1 M TBAHP$^{k)}$	0,73	32
CH_3	CH_3	CH_3	$C_{18}H_{37}S$		68 (hexane)	31		0,27 0,1 M TBAHP$^{k)}$	0,78	32
CH_3	CH_3	CH_3	$C_6H_5CH_2S$		127 (hexane)	57		0,27 0,1 M TBAHP$^{k)}$	0,81	32
CH_3	CH_3	CH_3	$C_2H_5OOC(CH_2)_{10}S$		59 (hexane)	41		0,27 0,1 M TBAHP$^{k)}$	0,77	32

(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

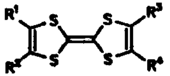


R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ϵ)	E_1^{Ox} [V]	E_2^{Ox}	references
CH_3	CH_3	CH_3	$C_2H_5OOC(CH_2)_{15}S$		71 (hexane)	32		0,27 0,1 M TBAHP[k]	0,78	32
H	H	$-O(CH_2)_2O-$		B Z=O $(EtO)_3P$	92	2,5	483, 296 - 308 sh, 246[a]			108
H	H	CH_3S	CH_3S	B $(EtO)_3P$	60		450, 370, 324, 306, 292[a]			192
H	H	$-SCH_2S-$		B $(EtO)_3P$	154	29	448, 370, 326, 307, 294[a]	0,54 0,025 M TBAHP[e]	0,92	192
H	H	$-S(CH_2)_2S-$		B $(EtO)_3P$	200	36	444, 363, 327, 306, 293[a]	0,55 0,025 M TBAHP[e]	0,97	192
H	H	$-S\underset{CH_3}{CH}-CH_2S-$		B $(EtO)_3P$	79	12	444, 365, 328, 306, 292[a]			192
H	H	$-S\underset{CH_3}{CH}-\overset{CH_3}{CH}S-$		B $(EtO)_3P$	146		442, 362, 321, 306, 290[a]			192

H	H	$-S(CH_2)_3S-$	B $(EtO)_3P$	151	33	450, 386, 322, 300$^{a)}$			192
H	H	$-SCH_2COCH_2S-$		179-182 dec. (cubes) 186-187 dec. (needles)			0,60 0,1 M TBAHP$^{g,v)}$	0,91	156
H	H	$-SeCH_2Se-$		173	21	450, 325, 306, 225$^{a)}$	0,49 0,025 M TBAHP$^{e)}$	0,87	193
H	H	$-Se(CH_2)_2Se-$		195	20	440, 368, 318, 290, 230$^{a)}$			193
H	H	$-Se(CH_2)_3Se-$		148	18	389, 323, 280, 225$^{a)}$			193
H	CH_3	$-S(CH_2)_2S-$					0,41 0,1 M TBAP	0,75	136
H	CH_2OH	$-S(CH_2)_2S-$		121-123 ($CHCl_3$/petroleum ether)	45		0,52* 0,1 M TBAP$^{q)}$	0,70*	194
H	$(CH_2)_3C=CH$	$-S(CH_2)_2S-$			75				195
H	$(CH_2)_8C=CH$	$-S(CH_2)_2S-$			75				195
H	$(CH_2)_3C\equiv C-C\equiv C(CH_2)_{11}CH_3$	$-S(CH_2)_2S-$		43-45			0,48 g,q)	0,68	195
H	$(CH_2)_8C\equiv C-C\equiv C(CH_2)_4CH_3$	$-S(CH_2)_2S-$		72-74			0,48 g,q)	0,68	195

(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

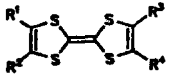


R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
H	$(CH_2)_8C\equiv C-C\equiv C(CH_2)_{11}CH_3$	$-S(CH_2)_2S-$			52-54			0,48 g,q)	0,68	195
CH_3	CH_3	$P(C_6H_5)_2$	$P(C_6H_5)_2$		162-163	75	420 (2 050), 324 (16 200)k)	0,34 0,1 M TBAHP	0,71	196
CH_3	CH_3S	CH_3S	CH_3		141 (heptane)	49		0,36 0,1 M TBAHPk)	0,72	32
CH_3	$C_{18}H_{37}S$	$C_{18}H_{37}S$	CH_3		85	40		0,35 0,1 M TBAHPk)	0,73	32
CH_3	CH_3	CH_3S	CH_3S					0,40 0,2 M TEAB	0,70	197
								0,40 0,1 M TBAP	0,73	136
CH_3	CH_3	$-SCH_2S-$			139-141					33
CH_2OH	CH_2OH	$-S(CH_2)_2S-$			170-175 (EtOAc)			0,53* 0,1 M TBAPq)	0,72*	194

CH_3	CH_3	$-SCH_2COCH_2S-$		220-222			0,51 0,1 M TBAHP[g,v]	0,96	156
CH_3	CH_3	$-SCH_2\underset{OH}{CH}CH_2S-$		207-210					156
$-O(CH_2)_2O-$		$-SCH_2S-$	B Z=O,S $(EtO)_3P$	171	3,9				182
$-O(CH_2)_2O-$		$-S(CH_2)_2S-$	B $(MeO)_3P$	184-185 dec.			0,01 0,1 M TBAHP[h,k]	0,43	198
			B Z=O $(EtO)_3P$	192	14	490, 445 sh, 324, 310 sh, 220 sh[a]			108
$-O(CH_2)_2O-$		$-SCH{=}CHS-$	B Z=O,S $(EtO)_3P$	194	4,5				182
$-O(CH_2)_2O-$		$-SeCH_2Se-$	B Z=O,S $(EtO)_3P$	218	< 1				182
$-O(CH_2)_2O-$		$-Se(CH_2)_2Se-$	B Z=O $(EtO)_3P$	187	4,5	486, 442 sh, 324, 310 sh, 230 sh[a]			108
$-O(CH_2)_2O-$		$-(CH{=}CH)_2-$	B Z=O,S $(EtO)_3P$	175	7				182

(Continued)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

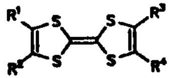


R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
CH_3S	CH_3S	C_4H_9S	C_4H_9S			54				98a
CH_3S	CH_3S	$C_{12}H_{25}S$	$C_{12}H_{25}S$		65-66					33
CH_3S	CH_3S	$C_{18}H_{37}S$	$C_{18}H_{37}S$		65-66					33
CH_3OOCCH_2S	CH_3OOCCH_2S	$C_{18}H_{37}S$	$C_{18}H_{37}S$	B Z=S $(EtO)_3P$	64-66	12	380 sh, 330, 310, 265$^{k)}$	0,7	0,96	199
p-$CH_3COOC_6H_4CH_2S$	p-$CH_3COOC_6H_4CH_2S$	CH_3S	CH_3S	B Z=O $(EtO)_3P$	80-85	30				98a
p-$CH_3COOC_6H_4CH_2S$	p-$CH_3COOC_6H_4CH_2S$	C_4H_9S	C_4H_9S	B Z=O $(EtO)_3P$	90-92	17				98a
CH_3S	CH_3S	$-SCH_2S-$			83	11	480, 384, 342, 313$^{a)}$			146
CH_3OOCCH_2S	CH_3OOCCH_2S	$-SCH_2S-$		B $(EtO)_3P$	87	20	480, 418, 340, 312, 298, 274$^{a)}$			146

CH_3S	$HO(CH_2)_8S$	$-SCH_2S-$		oil					33
CH_3S	$C_{18}H_{37}S$	$-SCH_2S-$		46-49					33
$C_{18}H_{37}S$	$C_{18}H_{37}S$	$-SCH_2S-$		65-67					33
$-S(CH_2)_2S-$		$-SCH_2S-$	B Z=O $(MeO)_3P$	183,5-184 ($CHCl_3$)			0,07 0,1 M TBAHP$^{h,k)}$	0,45	200
				184	19	495, 342, 319, 280, 226$^{a)}$			148
$-S(CH_2)_2S-$		$-SCHS-$ $COOCH_3$	B $(EtO)_3P$	167	29	478, 348, 319, 306, 230, 212$^{a)}$			148
$-SCH-CH_2S-$ CH_3		$-SCH_2S-$		166	16				148
$-SCH-CH_2S-$ CH_3		$-SCHS-$ $COOCH_3$	B $(EtO)_3P$	131	16				148
CH_3 $-SCH-CHS-$ CH_3		$-SCH_2S-$		167	8				148
CH_3 $-SCH-CHS-$ CH_3		$-SCHS-$ $COOCH_3$	B $(EtO)_3P$	141	21				148
$-S(CH_2)_3S-$		$-SCH_2S-$	B Z=O $(MeO)_3P$	192-193 dec.			0,08 0,1 M TBAHP$^{h,k)}$	0,46	201
				189	12				148

(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

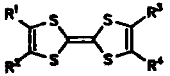


R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{0x} [V]	E_2^{0x} [V]	references
$-S(CH_2)_3S-$		$-SCHS-$ $COOCH_3$		B $(EtO)_3P$	178	18				148
CH_3S	CH_3S	$-S(CH_2)_2S-$		A	64 75	6 8		0,48 0,1 M TEAP	0,72	98a, 146, 202
CH_3S	CH_3S	$-SCH-CH_2S-$ CH_3			61	4				146
CH_3S	CH_3S	CH_3 $-SCH-CHS-$ CH_3			93	6				146
CH_3OOCCH_2S	CH_3OOCCH_2S	$-S(CH_2)_2S-$		B $(EtO)_3P$	96	16				146
CH_3OOCCH_2S	CH_3OOCCH_2S	$-SCH-CH_2S-$ CH_3		B $(EtO)_3P$	65	14				146
CH_3OOCCH_2S	CH_3OOCCH_2S	CH_3 $-SCH-CHS-$ CH_3		B $(EtO)_3P$	> 82	33				146

RS R: $(CH_3)_3Si(CH_2)_2OCH_2$	RS	$-S\underset{CH_3}{CH}-\overset{CH_3}{CHS}-$	B Z=0,S $(EtO)_3P$	oil		470, 375 sh, 312, 299 sh, 250 sh, 229[a)]			33
RS R: $(CH_3)_3Si(CH_2)_2OCH_2$	$BrCH_2CH_2S$	$-S\underset{CH_3}{CH}-\overset{CH_3}{CHS}-$		76-78		470, 378 sh, 337 sh, 312, 300 sh, 250 sh, 228[a)]			33
$ClCH_2CH_2S$	$ClCH_2CH_2S$	$-S(CH_2)_2S-$	B Z=0,S $(EtO)_3P$		27				88
$C_{12}H_{25}S$	$C_{12}H_{25}S$	$-S(CH_2)_2S-$	B Z=0 $(EtO)_3P$						203
$C_{18}H_{37}S$	$C_{18}H_{37}S$	$-S(CH_2)_2S-$	B Z=0 $(EtO)_3P$				0,63	0,94	199, 203
$-S(CD_2)_2S-$		$-S(CH_2)_2S-$		237-238					33
$-S(CH_2)_2S-$		$-S\underset{C_{16}H_{33}}{CH}-CH_2S-$	B Z=0 $(EtO)_3P$	92-93 (hexane)	13		0,63	0,90[a)]	154
							0,59	0,89[e)]	154
$-S(CH_2)_2S-$		$-S\underset{CH_3}{CH}-CH_2S-$		193-194					33
$-S(CH_2)_2S-$		$-S\underset{CH_3}{CH}-\overset{CH_3}{CHS}-$		212 $(CHCl_3)$	30	343 sh, 321, 230[a)]			33

(Continued)

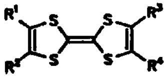
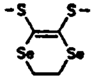
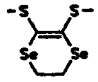
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)



R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
CH_3S	CH_3S	$-S(CH_2)_3S-$		A	124	17		0,48 0,1 M TEAP	0,73	146, 202
CH_3S	CH_3S	$-SCH_2COCH_2S-$			175-178			0,64 0,1 M TBAHP[g,v]	0,98	156
CH_3S	CH_3S	$-S(CH_2CH_2O)_3CH_2CH_2S-$		B Z=S $(EtO)_3P$	125-126 ($EtOH/CHCl_3$)	21		0,51	0,76[h,k]	145
CH_3OOCCH_2S	CH_3OOCCH_2S	$-S(CH_2)_3S-$		B $(EtO)_3P$	119	20				146
$-S(CH_2)_2S-$		$-S(CH_2)_3S-$			235-236 dec.			0,11 0,1 M TBAHP[h,k]	0,52	201
$-S(CH_2)_2S-$		$-SCH_2COCH_2S-$			218-220			0,64 0,1 M TBAHP[g,v]	1,02	156
$C_{18}H_{37}S$	$C_{18}H_{37}S$	$-Se(CH_2)_2Se-$		B Z=O $(EtO)_3P$	84	20				204

$C_{18}H_{37}S$	$C_{18}H_{37}S$	$-Se(CH_2)_3Se-$		B Z=O $(EtO)_3P$	80	17	204
$-SCH_2S-$		CH_3Se	CH_3Se		oil		33
$-SCH_2S-$		$-Se(CH_2)_2Se-$		B Z=O $(EtO)_3P$	285	11	204
$-SCH_2S-$		$-Se(CH_2)_3Se-$		B Z=O $(EtO)_3P$	212	14	204
$-S(CH_2)_2S-$		$C_{18}H_{37}Se$	$C_{18}H_{37}Se$	B Z=O $(EtO)_3P$	84	14	204
$-S(CH_2)_2S-$		$-SeCH_2Se-$		B Z=O $(EtO)_3P$	230	4	204
$-S(CH_2)_2S-$		$-Se(CH_2)_2Se-$			294	12	204
$-S(CH_2)_3S-$		$C_{18}H_{37}Se$	$C_{18}H_{37}Se$	B Z=O $(EtO)_3P$	86	17	204
$-S(CH_2)_3S-$		$-SeCH_2Se-$		B Z=O $(EtO)_3P$	230	8	204

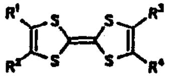
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

 R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
C_6H_5Se	C_6H_5Se	C_6H_5Se	H		84					83
$-SCH=CHS-$		H	H	B $(EtO)_3P$	181	18	440, 380, 323, 300[a)]			192
		H	H		220					173
		H	$COOCH_3$	B Z=S $(EtO)_3P$	141					173
$-SCH=CHS-$		CH_3S	CH_3S		117	7				146
$-SCH=CHS-$		CH_3OOCCH_2S	CH_3OOCCH_2S	B $(EtO)_3P$	107	12				146
$-SCH=CHS-$		$-SCH_2S-$			189	8				148
$-SCH=CHS-$		$-SCHS-$ $COOCH_3$		B $(EtO)_3P$	171-173	23				148
		$-O(CH_2)_2O-$		B Z=O,S $(EtO)_3P$	290	19	349 sh, 320, 274[k)]			173

$-SCH=CHS-$		$-S(CH_2)_2S-$							205
$-S\overset{CH_3}{C}=\underset{CH_3}{C}S-$		$-S(CH_2)_2S-$							205
$-SCH=CHS-$		$-Se(CH_2)_2Se-$		B Z=O $(EtO)_3P$	284	13			204
$-SCH=CHS-$		$-Se(CH_2)_3Se-$		B Z=O $(EtO)_3P$	231	8			204
$CH_2=CHS$	$CH_2=CHS$	$-S(CH_2)_2S-$			50-51		475, 380, 338 sh, 313, 300 sh, 227$^{a)}$	0,54 0,91 0,1 M TBAHP$^{g,k)}$	33, 88
CH_3S	CH_3S	$-CH=CH-CH=CH-$						0,55 0,83 0,2 M TEAB	197
CH_3S	CH_3S	H	$COOCH_3$	B $(EtO)_3P$			480, 418, 320, 302$^{a)}$		192
$-SCH_2S-$		H	$COOCH_3$	B $(EtO)_3P$	193	3	480, 408, 326, 303$^{a)}$		192
$-S(CH_2)_2S-$		H	$COOCH_3$	B Z=O,S $(MeO)_3P$		13			194
$-S(CH_2)_2S-$		CH_2OH	$COOCH_3$			70			194

(Continued)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

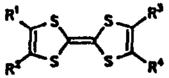
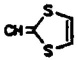
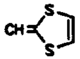


R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
-S(CH$_2$)$_3$S-		H	COOCH$_3$	B (EtO)$_3$P			482, 406, 321, 308$^{a)}$			192
CH$_3$S	CH$_3$S	COOCH$_3$	COOCH$_3$	B (EtO)$_3$P	83	35	434, 322, 294, 257$^{a)}$			192
C$_{18}$H$_{37}$S	C$_{18}$H$_{37}$S	COOCH$_3$	COOCH$_3$	B Z=S (EtO)$_3$P	75	18	440 sh, 370 sh, 325, 295, 260	0,76	1,02	199
-SCH$_2$S-		COOCH$_3$	COOCH$_3$	B (EtO)$_3$P	143	39	440, 332, 306, 270$^{a)}$			192
-S(CH$_2$)$_2$S-		CHO	CH(OC$_2$H$_5$)$_2$	I M=Co$_2$ n=8		13				194
-S(CH$_2$)$_2$S-		CHO	CHO		210-211 dec.					194
-S(CH$_2$)$_2$S-		COOCH$_3$	COOCH$_3$	B (EtO)$_3$P	119	30	430, 326, 305, 298$^{a)}$			192
				B Z=O,S (MeO)$_3$P		60				194

$-S(CH_2)_3S-$		$COOCH_3$	$COOCH_3$	B $(EtO)_3P$	165	22	430, 325, 288, 270$^{a)}$			192
$-\underset{CH_3}{SCH}-CH_2S-$		$COOCH_3$	$COOCH_3$	B $(EtO)_3P$	110	12	435, 327, 305, 292$^{a)}$			192
$-\underset{CH_3}{SCH}-\overset{CH_3}{CHS}-$		$COOCH_3$	$COOCH_3$	B $(EtO)_3P$		9	432, 328, 305, 295$^{a)}$			192
$-SCH{=}CHS-$		$COOCH_3$	$COOCH_3$	B $(EtO)_3P$	146	8	430, 322, 296, 227$^{a)}$			192
$-SeCH_2Se-$		H	$COOCH_3$	B $(EtO)_3P$	210	9	417, 326, 304, 294, 220$^{a)}$			193
$-SeCH_2Se-$		$COOCH_3$	$COOCH_3$	B $(EtO)_3P$	152	35	436, 330, 306, 264, 233$^{a)}$			193
$-Se(CH_2)_2Se-$		$COOCH_3$	$COOCH_3$	B $(EtO)_3P$	113	20	433, 326, 312, 296, 245, 229$^{a)}$			193
$-Se(CH_2)_3Se-$		$COOCH_3$	$COOCH_3$	B $(EtO)_3P$	159	18	428, 325, 295, 232$^{a)}$			193
H	H	Cl	Cl		103-106	4		0,70 0,01 M TBAP$^{g,k)}$	0,97	86
H	H	Br	Br		129-130	5		0,65 0,01 M TBAP$^{g,k)}$	0,95	86
					128,5-130,4					87

(*Continued*)

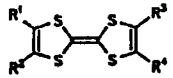
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

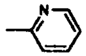
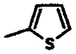
 R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} (ε) [nm]	E_1^{Ox} E_2^{Ox} [V]	references
H	H					82		0,22 0,30 0,1 M TBAP$^{q)}$	102
H	$COOC_4H_9$	$COOC_4H_9$	I		87-89	37	438 (2 515), 311 (14 450), 298 (13 200), 278 (13 200)$^{a)}$	0,71 1,01 0,1 M TEAP	101, 136
								0,76 1,06 0,1 M TBAP$^{g)}$	101
I	$COOC_4H_9$	$COOC_4H_9$	I		141-143		439 (2 550), 311 (15 850), 270 (17 800)$^{a)}$		101
H	$COOC_4H_9$	$COOC_2H_5$	$COOC_4H_9$					0,75 1,05 0,1 M TBAP$^{g)}$	101, 142
H	$COOC_4H_9$	$COOC_4H_9$	$COCH_3$		75-77	53	442 (3 550), 312 (21 400), 301 (23 450), 285 (23 450)$^{a)}$	0,76 1,14 0,1 M TBAP	101, 136
								0,81 1,13 0,1 M TBAP$^{g)}$	101
$COCH_3$	$COOC_4H_9$	$COOC_4H_9$	$COCH_3$		98-99 (hexane)		446 (2 040), 318 (12 900), 291 (17 400)$^{a)}$	0,86 1,17 0,1 M TBAP	101, 136

							0,91 0,1 M TBAP$^{g)}$	1,22	101
CH_3	CH_3	$COOCH_3$	$COOCH_3$				0,55 0,1 M TBAP	0,88	136
CH_3	CH_3	C_6H_5	C_6H_5				0,39 0,1 M TBAP	0,73	136
H	H	$-(CH=CH)_2-$					0,60 0,1 M TBAP$^{v)}$	0,94	191
CH_3	CH_3	$-(CH=CH)_2-$					0,50 0,1 M TBAP$^{v)}$	0,96	191
							0,47 0,1 M TBAP	0,89	136
$-(CH_2)_3-$		$-(CH=CH)_2-$		C	197		0,53 0,1 M TBAP$^{v)}$	0,98	191
$-(CH_2)_4-$		$-(CH=CH)_2-$					0,53 0,1 M TBAP$^{v)}$	1,00	191
H	H	H	$CHOHC_{17}H_{35}$		31-33	70			141
H	H	H	$CH_2N(CH_3)_2$		78-80	44	0,36 0,1 M TBAHP$^{k)}$	0,87	79
H	H	H	$CH_2N(CH_2)_5$		110-112	38	0,34 0,1 M TBAHP$^{k)}$	0,88	79

(*Continued*)

TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

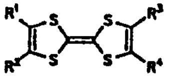


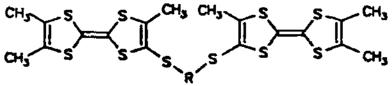
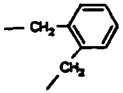
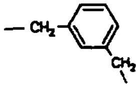
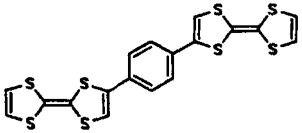
R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} E_2^{Ox} [V]	references
H	H	H	$CH_2N(CH_3)CH_2C_6H_5$		68-70	35		0,34 0,87 0,1 M TBAHP$^{k)}$	79
H	H	H	C_6H_5		79,5-81	67		0,38 0,80 0,1 M TBAP$^{e,g)}$	85
H	H	H	p-CNC_6H_4		210,5-213 dec.	98		0,47 0,87 0,1 M TBAP$^{e,g)}$	85
H	H	H	p-$CH_3OC_6H_4$		160-162 dec.	33		0,38 0,80 0,1 M TBAP$^{e,g)}$	85
H	H	H			173-175	82		0,39 0,85 0,1 M TBAP$^{e,g)}$	85
H	H	H			79-80	62		0,41 0,80 0,1 M TBAP$^{e,g)}$	85
H	H	H	$COOC_4H_9$					0,51 0,86 0,1 M TBAP	136, 142
H	H	H	$COOC_6H_{13}$		61-64	18			141

H	H	H	$COOC_8H_{17}$	60-62	15				141
H	H	H	$COOC_{16}H_{33}$	71-72	29				141
H	H	H	$CSOC_{16}H_{33}$	78-80	38	539, 315, $309^{k)}$	0,49	$0{,}86^{g,k)}$	141, 206
H	H	H	$COC_{15}H_{31}$	81	20		0,52	$0{,}90^{g)}$	141, 207
H	H	H	$COC_{17}H_{35}$	85	20				141, 208
H	H	H	$CO(CH_2)_3Br$	205 dec.	30				141
H	H	H	$CO(CH_2)_5Br$	114	27				141
H	H	H	$CO(CF_2)_6CF_3$	155-158	10				141
H	H	H	$CSC_{17}H_{35}$	71-76	50				141
H	H	H	$SCH{=}CH_2$	oil	53		0,45 0,1 M $TBAHP^{g,k)}$	(0,92)	88
H	H	H	$SCH_2CH_2OCOCH{=}CH_2$	oil			0,43 0,1 M $TBAHP^{g,k)}$	0,83	88
H	H	H	$SCH_2CH_2OCO\underset{CH_3}{C}{=}CH_2$	oil			0,43 0,1 M $TBAHP^{g,k)}$	0,89	88
H	H	H	$SC_{18}H_{37}$	55	13				141, 209
H	H	H	$SeC_{18}H_{37}$	52	15				141, 209

(Continued)

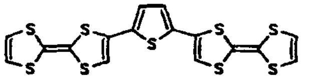
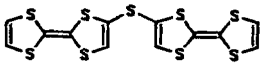
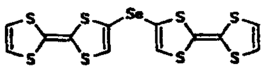
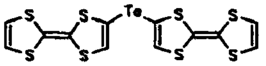
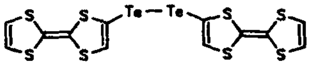
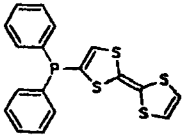
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

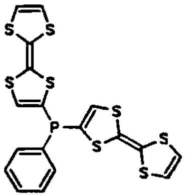
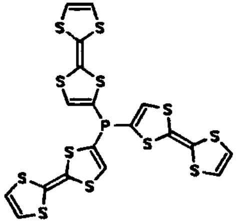
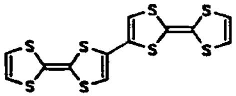
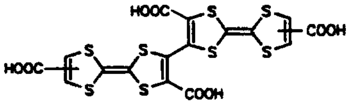
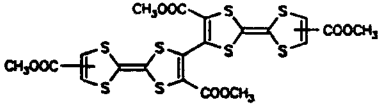
 R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
H	H	H	SeC_6H_5		98					83
H	H	H	$TeC_{18}H_{37}$		50	10				141, 209
H	H	H	$Si(CH_3)_3$		oil	26				141
H	H	H	$Si(CH_3)_2C_{18}H_{37}$		39-42	27				141
H	H	H	Cl					0,56 0,01 M $TBAP^{g,k)}$	0,78	86
H	H	H	Br		40-45 dec.	38		0,55 0,01 M $TBAP^{g,k)}$	0,76	86, 87
H	H	H	I		66-68 (hexane)		480 (302), 368 sh (1 590), 314 (10 700), 292 (9 330)$^{a)}$	0,45 0,1 M TBAP	0,83	101, 136
					110-112 dec.	34		0,55 0,01 M $TBAP^{g,k)}$	0,80	86
								0,50 0,1 M $TBAP^{g)}$	0,88	101

 R				
$-CH_2-$	250 (hexane)	24	0,22 0,36 0,80 0,1 M TBAHP$^{k)}$	32
$-(CH_2)_2-$	239 (hexane)	15	0,23 0,36 0,74 0,1 M TBAHP$^{k)}$	32
$-(CH_2)_3-$	196 (hexane)	33	0,28 0,75 0,1 M TBAHP$^{k)}$	32
$-(CH_2)_{10}-$	110 (hexane)	50	0,27 0,77 0,1 M TBAHP$^{k)}$	32
	229 (hexane)	23	0,29 0,79 0,1 M TBAHP$^{k)}$	32
	181 (hexane)	31	0,26 0,75 0,1 M TBAHP$^{k)}$	32
	253 (hexane)	35	0,28 0,76 0,1 M TBAHP$^{k)}$	32
	237-239 dec.	61	0,35 0,82 0,1 M TBAP$^{e,g)}$	85

(*Continued*)

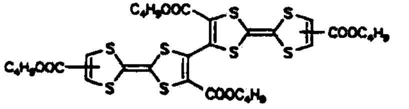
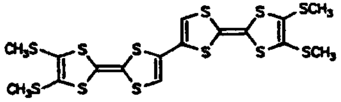
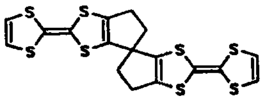
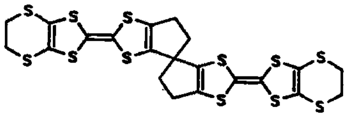
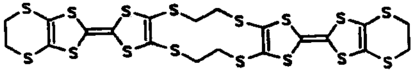
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

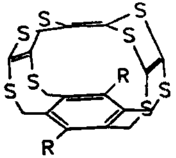
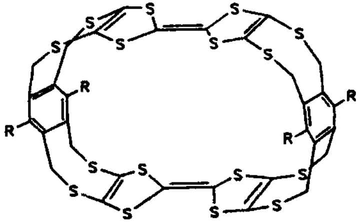
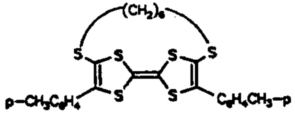
	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
		212-214 dec.	52		0,38 0,1 M TBAP$^{e,g)}$	0,81	85
		144-147 (CS$_2$/hexane)	14		0,49 (0,86) 0,1 M TEAHP$^{g,k)}$	0,61	84
		161-164	9		0,49 0,1 M TEAHP$^{g,k)}$	0,61	84
		176	20		0,31 0,1 M TBAP$^{g)}$	0,65	81, 82
			28				210
		41-43	51	388 (2 140), 312 (12 600), 254 (14 500)$^{k)}$	0,38 0,1 M TBAHP	0,74	196

	70-73	34	390 (3 150), 316 (19 700), 250sh (15 730)[k]	0,37 0,47 0,84 0,1 M TBAHP	196
	178-180	40	402 (5 750), 316 (35 800)[k]	0,47 0,86 0,1 M TBAHP	196
				0,35 0,47 0,54 0,86 0,1 M TBAHP[k]	196
				0,28 0,52 TBAHP[q]	80
	158-160 dec.		410 (7 250), 320 (22 400), 308 (21 400)[a]	0,45 0,65 0,97 0,1 M TBAP[g]	101
	225-226 dec.	62		0,43 0,84 0,1 M TBAP[e,g]	85
	> 250 dec.				101
	227-228 (benzene)		442 (3 710), 313 (19 050), 302 (18 200), 291 (16 200)[a]	0,85 1,13 0,1 M TBAP[g]	101

(*Continued*)

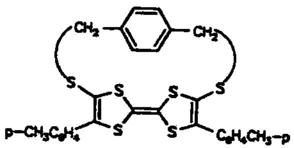
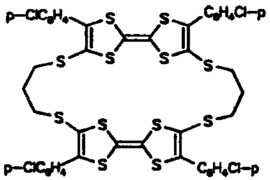
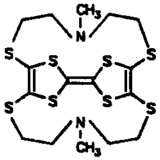
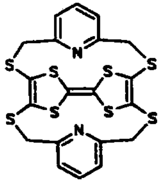
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

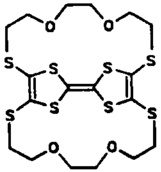
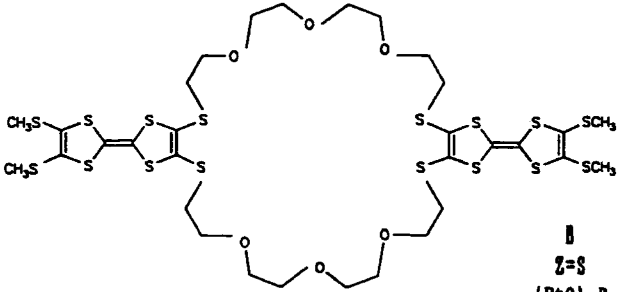
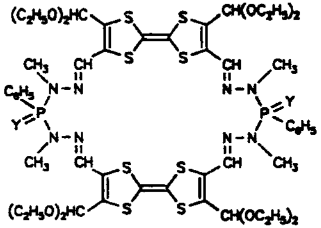
	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
			25	432 (6 025), 315 (38 000), 303 (36 300), 289 (33 900)[a]	0,83 0,1 M TBAP[g]	1,12	101
	B Z=O,S $(EtO)_3P$	172-173 ($CHCl_3$)	15		0,50 0,85 TBAP[k]	0,59	211
	A	> 200 dec. ($CHCl_3$)	18		0,41 0,66 TBAP[k]	0,50 0,78	212
	A	> 225 dec. (PhCl)	22		0,46 TBAP[k]	0,55 0,78	212
	B Z=O $(EtO)_3P$	239-242 dec. [$CCl_4(CS_2)$]			0,59 TBAP[g]	(0,84)	213

	R							
	O-Pr	B Z=S $(EtO)_3P$	227	38	393 sh (3 200), 311 (8 600), 228 (39 700)$^{k)}$	0,36 TBAHP$^{k)}$	1,03	165, 179, 213
	O-Bu	B Z=S $(EtO)_3P$	236	34				213
	O-Hex	B Z=S $(EtO)_3P$	205 dec. (EtOAc)	37	333 (3 473), 312 (4 297)$^{k)}$			165, 179, 213
		A		61				213
	OCOPent	B Z=O $(EtO)_3P$	186 dec.	59				213
		R						
		OPr		53		0,36 1,06 TBAHP$^{k)}$	1,01	166
		OBu		44				166
		OHex		47	422 (2 632), 330 (22 578), 307 (17 807), 227 (47 129)$^{k)}$			166
				72		(0,46) 0,1 M TBAT$^{g,k)}$		24

(*Continued*)

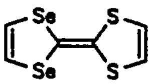
TABLE 3 (*Continued*)
Molecular properties of TTF (redox potential in acetonitrile vs. sce)

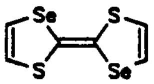
	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
			91		(0,46) 0,1 M TBAT$^{g,k)}$		24
			81		0,18 0,1 M TBAT$^{g,k)}$	0,45	24
	B Z=S (EtO)$_3$P	248-249 (CHCl$_3$/ MeOH)	31	344 (11 750), 265 (18 200), 241 (14 800)$^{w)}$	(0,95) TBAHP$^{k)}$		214
	B Z=S (MeO)$_3$P	90-92 dec. (CH$_2$Cl$_2$)	22	340 (7 080), 262 (16 600), 240 (16 200)$^{w)}$	0,27 0,1 M TBAP$^{g,v)}$	0,57	215

	B Z=S $(EtO)_3P$	247 $(EtOH/CHCl_3)$	22	338 (1 445), 304 (537), 259 (1 410)$^{w)}$	0,41 0,1 M TBAP$^{g,v)}$	0,73	162
	B Z=S $(EtO)_3P$	109-111 (MeCN)	8				145
		Y=O Y=S	80 60		0,61* 0,1 M TBAP$^{v)}$	1,05*	103

2. SYNTHESIS OF DISELENADITHIAFULVALENES (DSDTF)

DSDTF exist in two isomeric forms; in the isomer **16** each ring contains identical heteroatoms (1,3-diselena-6,8-dithiafulvalenes), in the isomer **17** each ring contains different heteroatoms (1,6-diselena-3,8-dithiafulvalenes) with the possibility of a cis and a trans form.


16

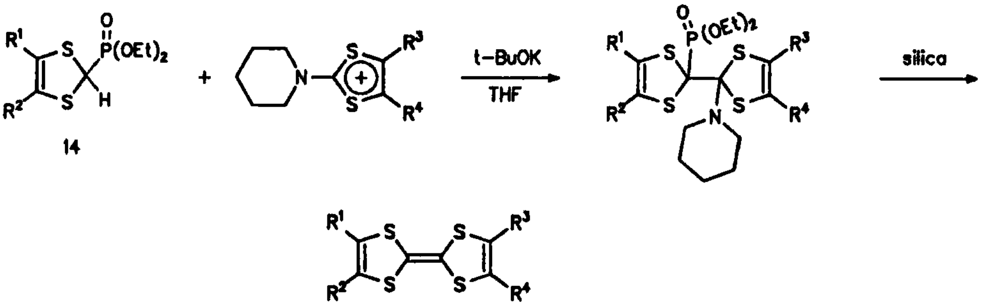

17

The 1,6-diselena-3,8-dithiafulvalenes are synthesized by reaction of 1,3-thiaselenole-2-thiones or -selones with trivalent phosphorus compounds.

The 1,3-diselena-6,8-dithiafulvalenes 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 DSDTF 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.[43,44]

In analogy to the synthesis of unsymmetrical TTF derivatives[36] the DSDTF are obtained in a pure form and without by-products of TTF and TSF by reaction of (1,3-dithiol-2-yl)ethyl phosphonate **14** with 2-amino-1,3-diselenolium salts in the presence of strong bases, followed by addition of acetic acid.[45–47]

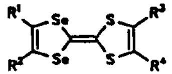
DSDTF and their data are summarized in Table 4.



3. SYNTHESIS OF TETRASELENAFULVALENES (TSF)

A precursor of TSF, 4,5-diselenolato-1,3-diselenole-2-selone, is formed not only by electrochemical reduction of carbon diselenide but also by reduction of carbon diselenide with sodium metal in organic solvents. The 4,5-diselenolato-1,3-di-

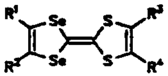
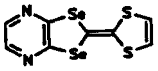
TABLE 4
Molecular properties of DSDTF (redox potential in acetonitrile vs. sce)



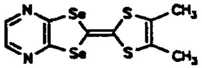
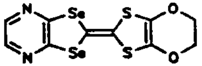
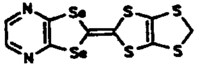
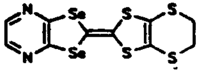
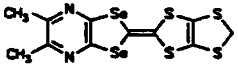
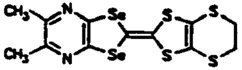
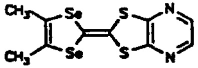
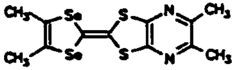
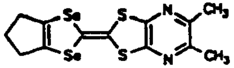
R^1	R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
CH_3	CH_3	CH_3	CH_3			25				45, 47
CH_3	CH_3	$-(CH_2)_4-$				10				47
$-(CH_2)_4-$		CH_3	CH_3			20				47
$-(CH_2)_4-$		$-(CH_2)_4-$				8				47
H	H	$-O(CH_2)_2O-$		B Z=O $(EtO)_3P$	> 90	< 1	492, 302, 248[a)]			108
H	H	$-SCH_2S-$			158					216
H	H	$-S(CH_2)_2S-$			207					216
CH_3	CH_3	$-SCH_2S-$			176-177					33
CH_3	CH_3	$-S(CH_2)_2S-$			198		490 (645), 340 sh (6 020), 313 (15 130), 208 (19 500)[a)]	0,52 0,1 M TBAP	0,78	44

(*Continued*)

TABLE 4 (*Continued*)
Molecular properties of DSDTF (redox potential in acetonitrile vs. sce)

R^1	 R^2	R^3	R^4	preparative method	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
					204-205 (pyridine)	5	485 (575), 397 (2 190), 346 (6 910), 307 (12 000)$^{v)}$			43
$-(CH_2)_3-$		$-S(CH_2)_2S-$			214		480 (302), 355 sh (6 310), 315 (14 120), 209 (19 500)$^{a)}$	0,48 0,1 M TBAP	0,73	44
CH_3	CH_3	$-S(CH_2)_3S-$			232		380 (1 480), 336 (7 580), 300 (14 800), 212 (19 950)$^{a)}$	0,48 0,1 M TBAP	0,75	44
$-(CH_2)_3-$		$-S(CH_2)_3S-$			234		378 (1 480), 332 (7 750), 303 (15 850), 208 (21 400)$^{a)}$	0,44 0,1 M TBAP	0,74	44
H	H	$-Se(CH_2)_2Se-$		B Z=O $(EtO)_3P$	210	20	486, 360 sh, 297 - 320 sh, 240 sh$^{a)}$			108
				B $(EtO)_3P$	174		418$^{a)}$			184

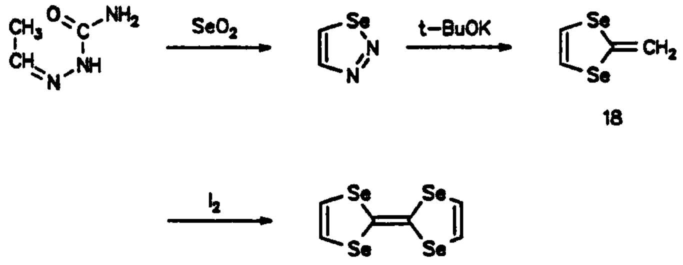
(*Continued*)

	B (EtO)$_3$P	180		418$^{a)}$			184
	B Z=O (EtO)$_3$P	210	5,5	410, 298 - 314 sh, 244 sh, 218$^{a)}$			108
	B (EtO)$_3$P	218	7	400$^{a)}$	0,69 0,1 M TEAP	0,96	184, 187
	B (EtO)$_3$P	229	25	405$^{a)}$	0,74 0,1 M TEAP	1,03	184, 187
	B (EtO)$_3$P	218	10	380$^{a)}$	0,66 0,1 M TEAP	0,92	184, 187
	B (EtO)$_3$P	238	18	386$^{a)}$	0,59 0,1 M TEAP	0,99	184, 187
	B (EtO)$_3$P	282	10	415$^{a)}$	0,69 0,1 M TEAP	1,02	184, 187
	B (EtO)$_3$P	302	1	405$^{a)}$	0,63 0,1 M TEAP	0,93	184, 187
	B (EtO)$_3$P	220		414$^{a)}$			184

(Continued)

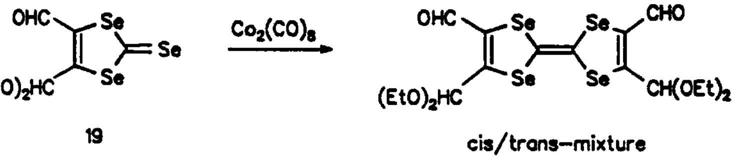
selenole-2-selone is isolated as bis(tetraphenylphosphonium) bis(2-selono-1,3-diselenole-4,5-diselenolato)zincate(II) in a yield of 15% in diglyme and 2% in dimethyl sulfoxide.[48] This complex is also formed by reaction of 1,3-diselenole-2-selone with LDA, selenium and subsequent treatment with zinc chloride and tetraphenylphosphonium bromide.[49]

In a yield of about 30% TSF is obtained without use of toxic CSe_2 in a three-step reaction. Acetaldehyde semicarbazone forms with selenium dioxide 1,2,3-selenadiazole, which reacts with potassium *t*-butoxide in DMF/*t*-BuOH and provides the fulvene **18**. Addition of a mixture of iodine and morpholine in DMF to a solution of **18** furnishes TSF.[50]



In analogy to the synthesis of TTF[51] the corresponding TSF are formed upon reflux of 1,3-diselenole-2-selones in toluene with dicobalt octacarbonyl. In the case of the monoacetalized **19** a mixture of practically equal amounts of the cis and trans isomer of the TSF is obtained and separated by silica thick layer chromatography.[52] The stereochemistry was assigned by analogy with the X-ray structures of the corresponding TTF.[53]

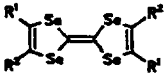
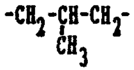
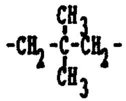
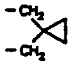
TSF and their data are summarized in Table 5.



4. SYNTHESIS OF TETRATELLURAFULVALENES (TTeF)

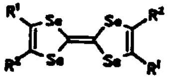
The synthesis of TTeF has been improved by the development of a five-step, one-pot reaction starting from *cis*-1,2-bis(trimethylstannyl)-ethylene.[54,55] After two consecutive metallations the 1,2-dilithioditelluraethylene formed (trapping with *cis*-$Pt(PPh_3)_2Cl_2$ gives $Pt(Te_2C_2H_2)(PPh_3)_2$ in 28% yield) was treated not with tetrachloroethylene,[54] but with tetrabromoethylene.[55] This greatly improves the ease of isolation, lowers the yield of undesirable by-products, and increases the

TABLE 5
Molecular properties of TSF (redox potential in acetonitrile vs. sce)

R^1 	R^2	Z	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
H	$COOCH_3$			85				217
H	COOH			62				217
$-(CH_2)_3-$						0,18 0,1 M TBAT[h,y]	0,45	218
 $-CH_2-\underset{CH_3}{CH}-CH_2-$				5		0,15 0,1 M TBAT[h,y]	0,39	218
 $-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-$				9		0,16 0,1 M TBAT[h,y]	0,39	219
				10		0,17 0,1 M TBAT[h,y]	0,41	218
CH_2OH	CH_2OH		247 dec.	53		0,48 0,1 M TBAP[q]	0,70	52
CHO	CHO		315 dec.	85				52

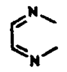
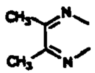
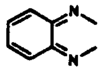
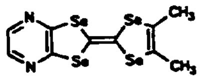
(*Continued*)

TABLE 5 (*Continued*)
Molecular properties of TSF (redox potential in acetonitrile vs. sce)



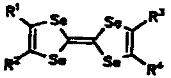
R^1	R^2	Z	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
CHO	$CH(OC_2H_5)_2$	I $M=Co_2$ n=8	153-157 173-176	35	466 (3 100), 286 (22 500)$^{k)}$ cis-isomer 472 (3 670), 286 (30 100)$^{k)}$ trans-isomer			52
COOH	COOH		> 300	28	360 (3 890), 322 (6 450), 277 (8 320), 205 (12 900)$^{p)}$			99
$CONH_2$	$CONH_2$			87				217
CH_2=CH	CH_2=CH		124,5-126			0,71 0,1 M TBAP$^{c)}$	0,89	52
CH_3S	CH_3S		119-119,7 (benzene/hexane)	66	492, 360, 305$^{a)}$	0,64 0,1 M TBAT	0,84	100
						0,78 0,1 M TBAT$^{n)}$	1,03	96
C_6H_5S	C_6H_5S		140 dec.	44	386 (795), 277 (5 250), 241 (7 950), 216 (8 320)$^{p)}$			99

(*Continued*)

CH_3Se	CH_3Se		112-113	10	430, 308, 280[a)]	0,58 0,1 M TEAP	0,81	220
			115,2-116,2	43		0,62 0,1 M TBAT	0,86	100
						0,75 0,1 M TBAT[n)]	1,04	96
C_6H_5Se	C_6H_5Se		155 dec.	52	388 (1 620), 297 (6 610), 219 (13 820)[p)]			99
		S $(EtO)_3P$	> 310		384			187, 188
			296 dec.	71				52
		O $(EtO)_3P$	> 310		378			187
		S $(EtO)_3P$						188
		O $(EtO)_3P$	258		407[a)]			184

(*Continued*)

TABLE 5 (*Continued*)
Molecular properties of TSF (redox potential in acetonitrile vs. sce)



R^1	R^2	R^3	R^4	Z	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E^{Ox}_1 [V]	E^{Ox}_2	references
H	H	$-(CH_2)_4-$			130			0,58 0,1 M TBAP$^{V)}$	0,96	191
$-(CH_2)_3-$		$-(CH_2)_4-$			223			0,50 0,1 M TBAP$^{V)}$	0,90	191

purified yield of TTeF to 12% (tetrachloroethylene gives a 5% yield of pure TTeF and tetraiodoethylene < 1% yield of pure TTeF).

One by-product in the reaction of 1,2-dilithioditelluraethylenes with tetrachloroethylene is the corresponding 1,4,5,8-tetratelluratetraline **20**.[54,56]

TTeF and their data are summarized in Table 6.

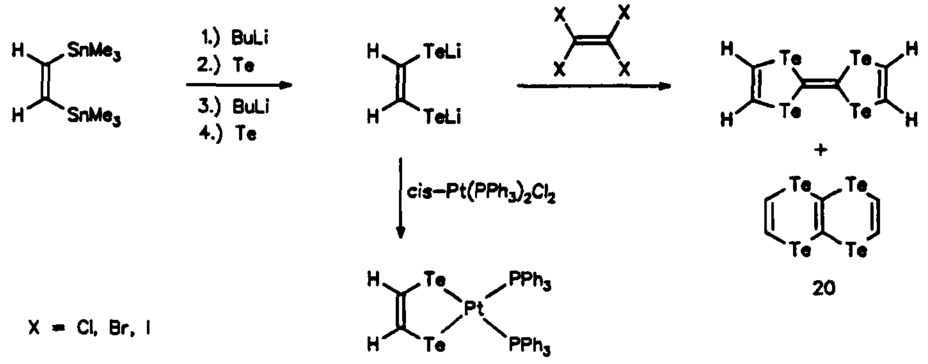
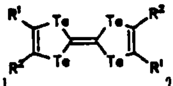
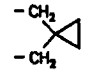
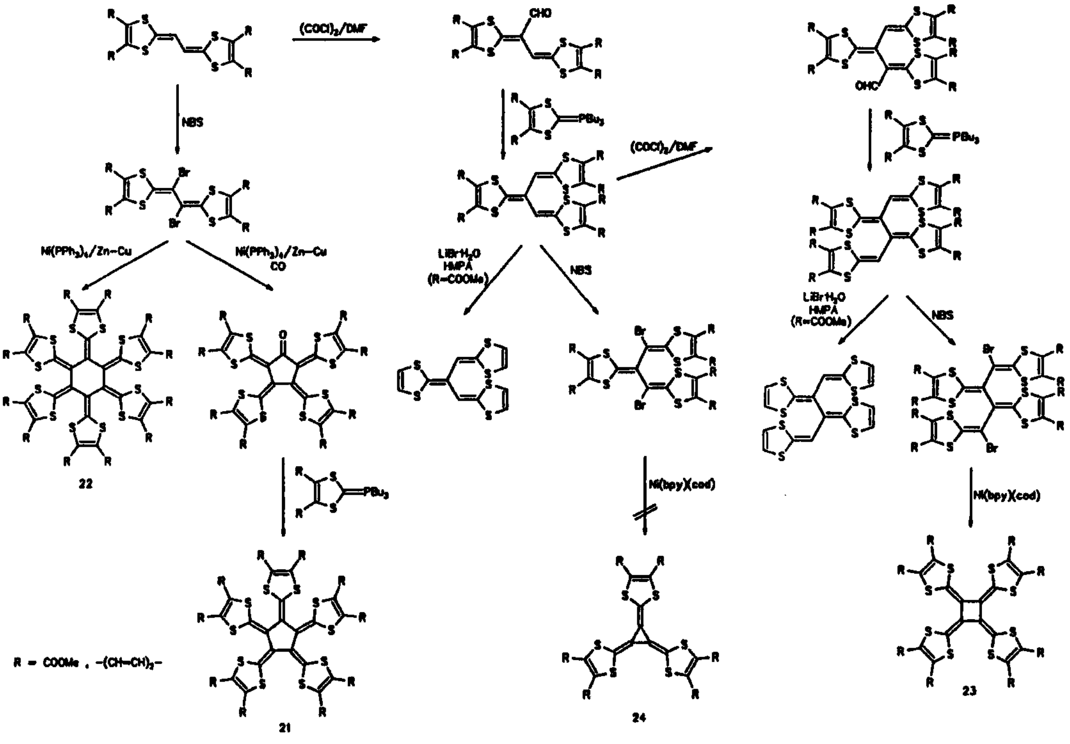


TABLE 6
Molecular properties of TTeF

 R^1	R^2	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm]	(ε)	E_1^{Ox} [V]	E_2^{Ox}	references
H	H			324		0,59 0,2 M TBAT[k)]	0,84	54, 55
$-CH_2-\underset{CH_3}{CH}-CH_2-$			20			0,08 0,1 M TBAT[h,y)]	0,34	218
$-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-$			35			0,10 0,1 M TBAT[h,y)]	0,31	218, 219
						0,11 0,1 M TBAT[h,y)]	0,34	219

5. SYNTHESIS OF CONJUGATED TETRATHIA- AND TETRASELENAFULVALENES

Some new TTF analogs have been synthesized with two or more 1,3-dithiol-2-ylidene moieties separated by olefinic bonds.[57,58] Starting from ethanediylidene-2,2′-bis(1,3-dithioles) [5]- and [6]-radialene **21** and **22** (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.[59–61] Reaction of the substituted tris(1,3-dithiol-2-ylidene)propane and tetrakis(1,3-dithiol-2-ylidene)butane (R = COOMe) with LiBr·H_2O in HMPA afforded the unsubstituted derivatives, both in 80% yield (Scheme 2).[62]

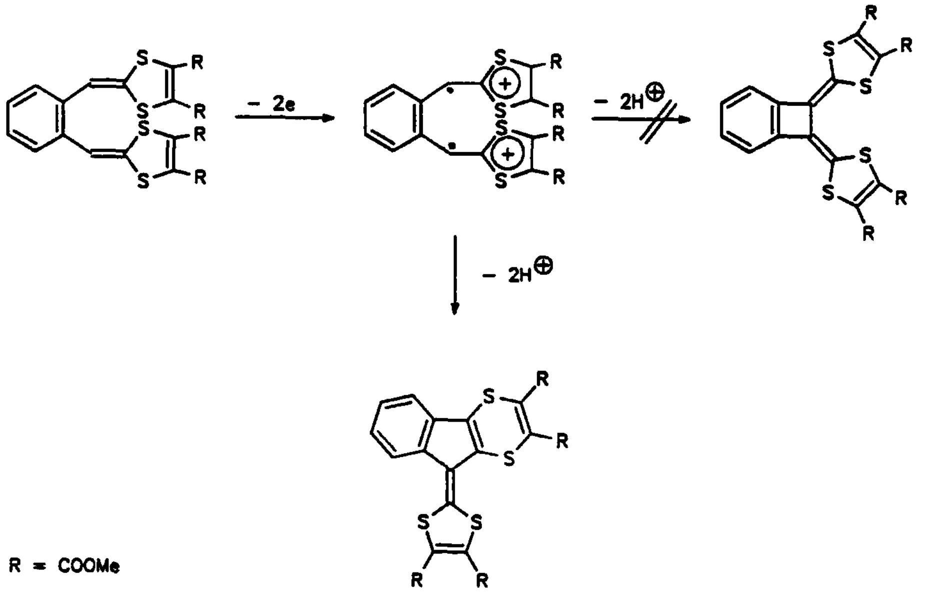


The [4]-radialene **23** (R = COOMe) is obtained in very low yield (3%) by two consecutive Vilsmeier reactions with oxalyl chloride/DMF and Wittig reactions with a phosphorane, then bromination with *N*-bromosuccinimide and treatment with a zero valent Ni(bpy)(cod)-complex.[62]

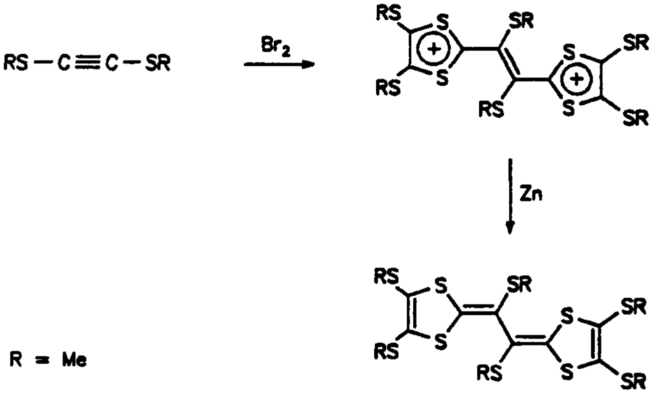
The [3]-radialene **24** (R = COOMe, -(CH=CH)$_2$-) has not yet been prepared in this way.[62]

X-Ray structure analyses of the [4]-, [5]- and [6]-radialenes indicated not a planar, but a three-dimensional structure.[59] Bromination of 1,2-xylene-α, α′-didylidenebis(4,5-dicarbomethoxy-1,3-dithiole) with bromine in carbon tetrachloride does not lead analogously to oxidation of diphenyldithiafulvene to a benzocyclobutene-derived molecule, but provides the dithiinofulvenetetraester **25**.[63]

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.[63a] An extension of the π-system between the

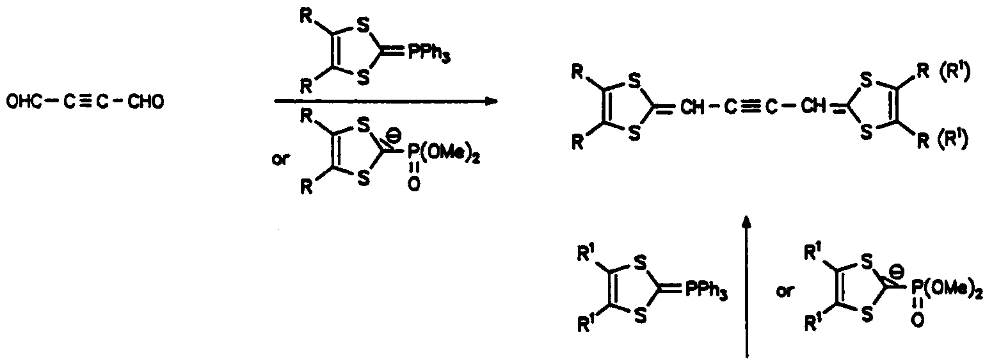


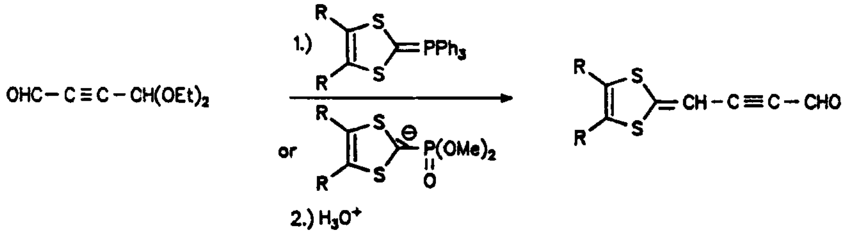
25



two 1,3-dithiol-2-ylidene moieties can also be achieved with olefinic and acetylenic bonds.

The Wittig or Wittig-Horner reaction of acetylenedicarbaldehyde with phosphoranes or phosphonate anions, respectively, generates the symmetrical acetylenic analogs of TTF.[64,65] From the mono(diethyl acetal) the unsymmetrical acetylenic analogs of TTF can be obtained. The yields are increased when complexes of the dialdehyde or the mono(diethyl acetal) with dicobalt hexacarbonyl are



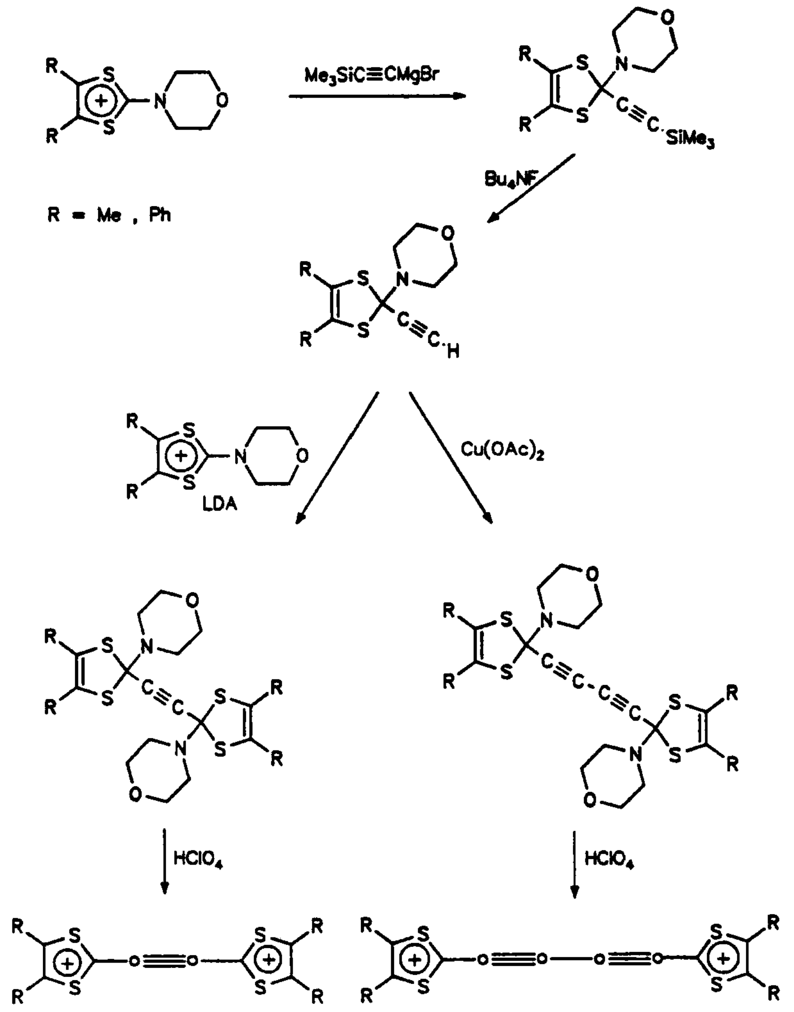


$R = H, Me, -(CH_2)_3-, -(CH_2)_4-, COOMe, -(CH{=}CH)_2-$
$R^1 = H, Me, -(CH_2)_3-, -(CH_2)_4-, -(CH{=}CH)_2-$

used as starting material instead of the corresponding free alkynes. The final decomplexation is achieved by treatment with trimethylamine oxide.[66]

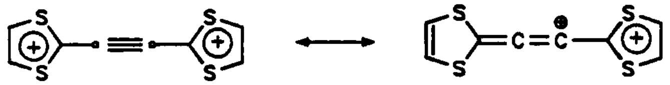
A cumulene skeleton has been inserted between the 1,3-dithioles in **26** and **27**. These TTF derivatives are formed by treatment of 2-morpholino-1,3-dithiolium salts with (trimethylsilyl)acetylene-magnesium bromide, followed by hydrolytic removal of the trimethylsilyl group. The dithiole thus obtained can be coupled with the starting 2-morpholino-1,3-dithiolium salts or dimerized in the presence of cupric acetate. Removal of the morpholino substituent by perchloric acid provides the cumulenic TTF.[67] So far only the dications **26** and **27** could be isolated in fairly good yields (70–90%). The neutral form is extremely unstable. Both positive charges are more located in the two 1,3-dithiolium units than in the corresponding ethanediylidene units.

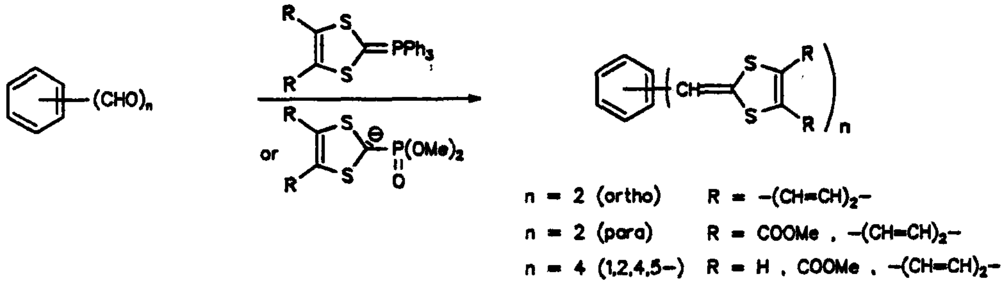
Probably π-conjugation between the 1,3-dithiolium units is less effective through an acetylenic than through an olefinic bond. Via a Wittig-Horner reaction, TTF derivatives are obtained with double bonds of olefinic and aromatic character between the two 1,3-dithiol-2-ylidene moieties in yields of 40–90%.[68] The *p*-derivative **28** with n = 2 (R = -(CH=CH)$_2$-) is also formed by reaction


Me$_3$SiC≡CMgBr
R = Me , Ph
Bu$_4$NF
LDA
Cu(OAc)$_2$
HClO$_4$
HClO$_4$
C≡C-SiMe$_3$
C≡C-H

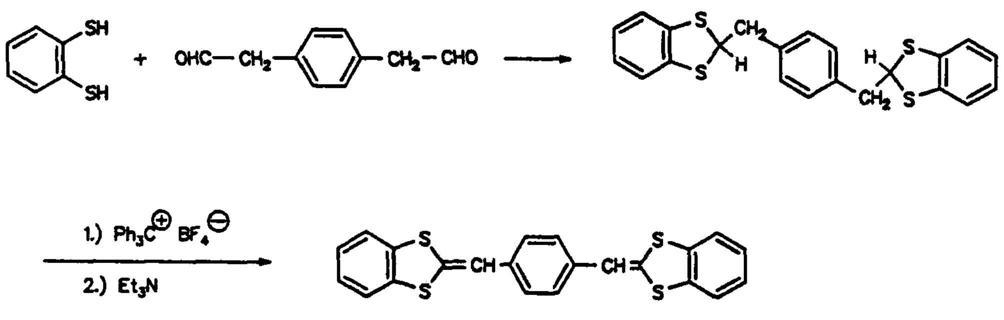
26

27

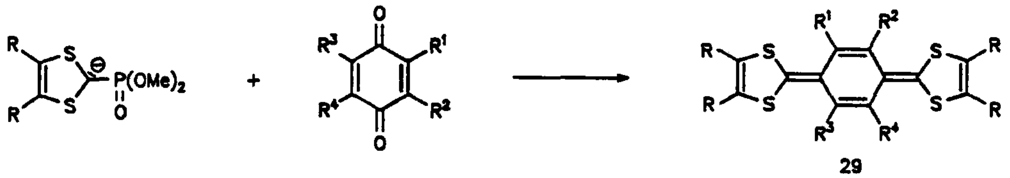




of benzene-1,2-dithiole with *p*-phenylenediacetaldehyde, subsequent hydride abstraction with trityl tetrafluoroborate and deprotonation with triethylamine.[58] Quinodimethane analogs **29** of TTF have been synthesized by Wittig or Wittig-Horner reaction of quinones with phosphoranes or phosphonate anions, respectively.

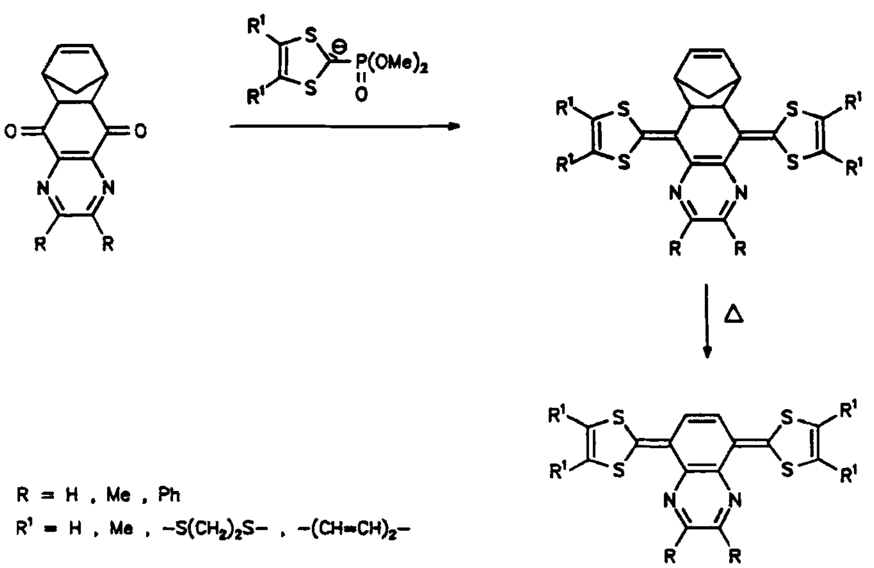


28



29

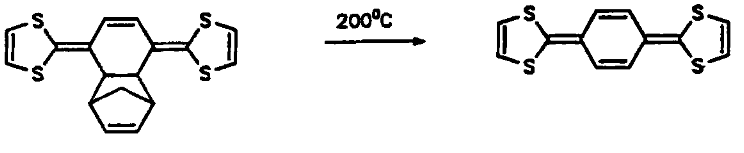
A number of annelated or heterocyclic fused quinoid structures have also been prepared in this way.[69–72] Pyrazine fused derivatives **30** are quantitatively obtained by a retro-Diels-Alder reaction of cyclopentadiene adducts which were synthesized by the above procedure.[73,74]



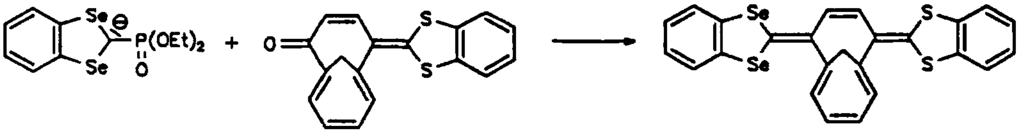
R = H , Me , Ph
R' = H , Me , –S(CH$_2$)$_2$S– , –(CH=CH)$_2$–

30

In this way the unsubstituted quinodimethane analog of TTF could be prepared for the first time in 54% yield.[75] Some other benzo- and naphtho-condensed

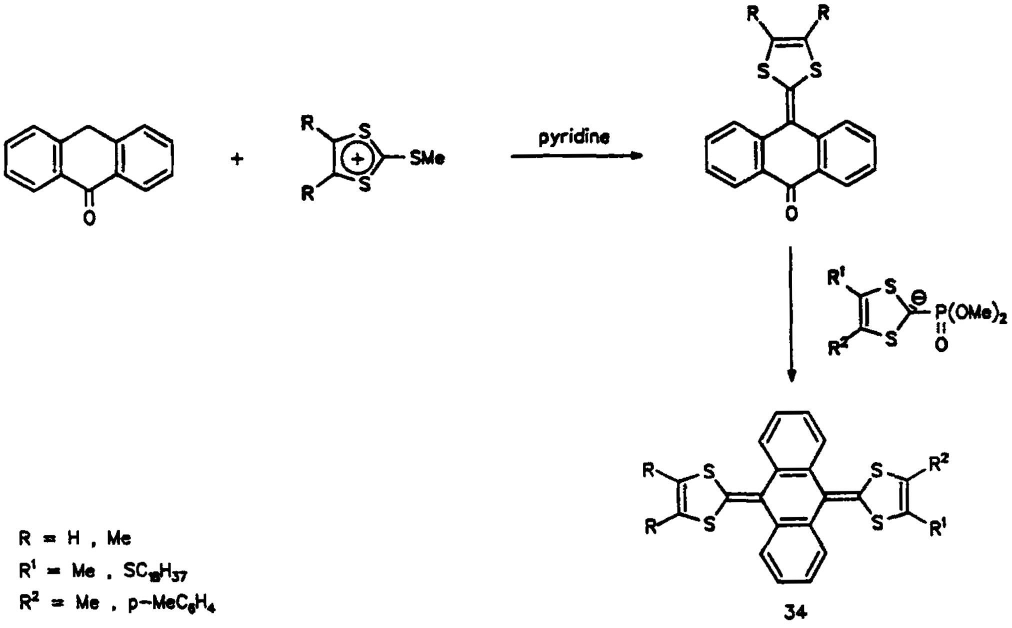


quinodimethane analogs of TTF have also been obtained by this retro-Diels-Alder reaction.[75] The Wittig-Horner reaction is also successful; treatment of the (1,3-diselenol-2-yl)phosphonate anion **31** with the ketone **32** provides, in quantitative yield, the vinylogous DSDTF **33**.[76]



31 32 33

Asymmetrically substituted quinoid analogs of TTF **34** 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.



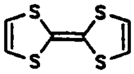
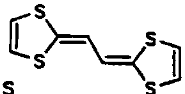
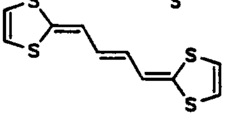
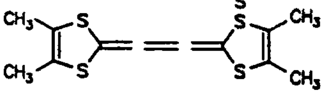
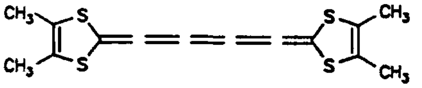
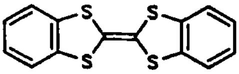
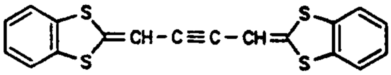
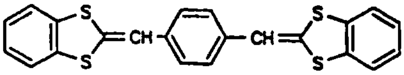
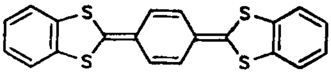
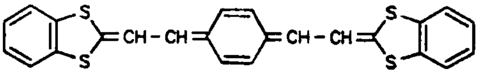
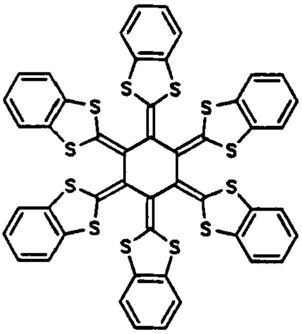
R = H, Me
R^1 = Me, SC$_{18}$H$_{37}$
R^2 = Me, p-MeC$_6$H$_4$

34

Use of a 1,3-thiaselenole phosphonate anion as the starting material afforded selenatrithiafulvalenes.[77] As mentioned above and demonstrated in Table 1, TTF derivatives with 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. 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 one-site Coulomb repulsion is greatly reduced. 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. Vinylogous, cumulenic, acetylenic, and quinoid TTF and TSF and their data are summarized in Table 7.

Table 1

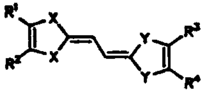
Oxidation potentials of vinylogous, cumulenic, acetylenic, and quinoid tetrathiafulvalenes in acetonitrile (vs. Ag/AgCl electrode, 0,1 M Et_4NClO_4 or 0,1 M Bu_4NClO_4)

Compound	E_1^{Ox} (V)	E_2^{Ox} (V)	references
	0,34	0,71	57
	0,20	0,36	57
	0,22		57
	(0,07)	(0,31)[a]	67
	(– 0,12)	(0,25)[a]	67
	0,72	1,06	58
	0,67	1,02[b]	65
	0,64	0,78	58
	0,27		58
	0,40		58
	0,43	(0,65)[c]	59

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

TABLE 7

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



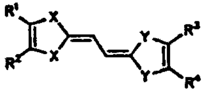
R^1	R^2	R^3	R^4	X	Y	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
H	H	CH_3	CH_3	S	S	151-152 dec. (benzene)	86		0,23 0,1 M TEAP[g)]	0,39	57
CH_3	CH_3	CH_3	CH_3	S	S				0,19 0,1 M TEAP[g)]	0,34	57
CH_3	CH_3	$COOCH_3$	$COOCH_3$	S	S	147-148 (CH_2Cl_2/hexane)	71		0,38 0,1 M TEAP[g)]	0,59	57
$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	S	S				0,60 0,1 M TEAP[g)]	0,74	57
C_6H_5	C_6H_5	C_6H_5	C_6H_5	S	S	180 dec. (benzene)	80		0,28 0,1 M TEAP[g)]	0,46	57
H	H	$-(CH=CH)_2-$		S	S				0,37 0,1 M TEAP[g)]	0,53	57
CH_3	CH_3	$-(CH=CH)_2-$		S	S	202-203 (benzene)	69		0,33 0,1 M TEAP[g)]	0,50	57

$COOCH_3$	$COOCH_3$	$-(CH=CH)_2-$		S	S				0,49 0,1 M TEAP g)	0,64	57
H	H	CH_3S	CH_3S	S	S	oil			0,40 0,1 M TEAHP g,k)	0,63	221
H	H	$C_{18}H_{37}S$	$C_{18}H_{37}S$	S	S	68-69			0,40 0,1 M TEAHP g,k)	0,63	221
H	H	$-S(CH_2)_2S-$		S	S	158	57	417 (20 900) u)	0,40 TBAHP	0,57	222
						161-162 (CH_2Cl_2/cyclohexane 1:3)	80	415, 401, 237, 197 k)	0,43 0,1 M TEAHP g,k)	0,69	223
H	H	$-S(CH_2)_3S-$		S	S	157-158	70		0,41 0,1 M TEAHP g,k)	0,64	221
CH_3	CH_3	CH_3S	CH_3S	S	S	106-107			0,33 0,1 M TEAHP g,k)	0,57	221
CH_3	CH_3	$-S(CH_2)_2S-$		S	S	201-202 (CH_2Cl_2/cyclohexane 1:3)	82	423, 401, 233, 197 k)	0,36 0,1 M TEAHP g,k)	0,62	223
CH_3	CH_3	$-S(CH_2)_3S-$		S	S	229-230	70		0,34 0,1 M TEAHP g,k)	0,61	221
CH_3	CH_3	$-Se(CH_2)_2Se-$		S	S	198-200	62		0,29 0,1 M TEAHP g,k)	0,54	224

(Continued)

TABLE 7 (*Continued*)

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



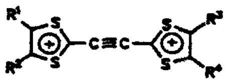
R^1	R^2	R^3	R^4	X	Y	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
$COOCH_3$	$COOCH_3$	$-S(CH_2)_2S-$		S	S	142 (toluene)	55		0,58 TBAHP	0,76	222
CH_3S	CH_3S	CH_3S	CH_3S	S	S	99			0,43 0,1 M TEAHP$^{g,k)}$	0,59	221
CH_3S	CH_3S	$-S(CH_2)_2S-$		S	S	137-139			0,42 0,1 M TEAHP$^{g,k)}$	0,62	221
CH_3S	CH_3S	$-S(CH_2)_3S-$		S	S	151-152	70		0,43 0,1 M TEAHP$^{g,k)}$	0,63	221
$-SCH_2S-$		$-SCH_2S-$		S	S	246-247 dec. (DMSO)	16		0,41 0,1 M TBAHP$^{k)}$	0,60	225
$-S(CH_2)_2S-$		$-S(CH_2)_2S-$		S	S	> 250 dec. (PhCN)	82	430 (14 120), 408 (13 500)$^{t)}$	0,36	0,59	226
						245 dec. (DMSO)	80	452 (37 200), 428 (36 300), 389 (33 100)$^{u)}$	0,40 0,1 M TBAHP$^{k)}$	0,57	222, 225

						239-240 (CS_2/hexane 2:1)	85	429, 403, 261 230, 197[k)]	0,48 0,1 M TEAHP[g,k)]	0,71	223
$-S(CH_2)_2S-$		$-S(CH_2)_3S-$		S	S	219-220	70		0,48 0,1 M TEAHP[g,k)]	(0,67)	221
$-S(CH_2)_3S-$		$-S(CH_2)_3S-$		S	S	247-249	70		0,47 0,1 M TEAHP[g,k)]	(0,68)	221
CH_3S	CH_3S	CH_3Se	CH_3Se	S	S	120-122	76		0,39 0,1 M TEAHP[g,k)]	0,57	224
CH_3Se	CH_3Se	CH_3Se	CH_3Se	S	S	132-134	58		0,39 0,1 M TEAHP[g,k)]	0,59	224
CH_3Se	CH_3Se	$-Se(CH_2)_2Se-$		S	S	123-125	65		0,35 0,1 M TEAHP[g,k)]	0,56	224
$-Se(CH_2)_2Se-$		$-Se(CH_2)_2Se-$		S	S	> 340 (CS_2/MeOH)	55		0,41 0,1 M TEAHP[g,k)]	0,63	224
$COOCH_3$	$COOCH_3$	H	H	S	Se	120 (CH_2Cl_2/ hexane)	63	403 sh (13 942), 383 (18 810), 231 (11 250)[k)]			227
$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	S	Se				0,62 0,1 M TEAP[g)]	0,77	57
$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	Se	Se				0,64 0,1 M TEAP[g)]	0,81	57

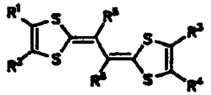
(*Continued*)

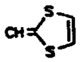
TABLE 7 (*Continued*)

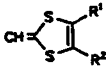
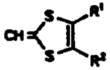
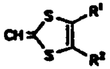
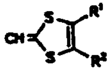
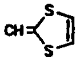
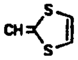
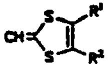
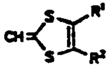
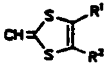
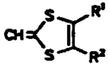
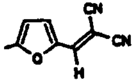
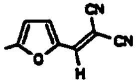
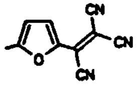
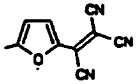
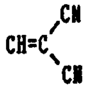
Molecular properties of vinylogous, cumulenic, acetylenic, and quinoid TTF and TSF (redox potential in acetonitrile vs. sce)



R^1	R^2	R^3	R^4	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
CH_3	CH_3	CH_3	CH_3		89	454 (19 500), 424 sh (14 800)$^{j)}$	(0,07) 0,1 M TBAP$^{g)}$	(0,31)	67
C_6H_5	C_6H_5	C_6H_5	C_6H_5		73				67



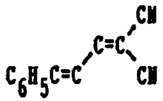
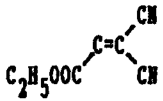
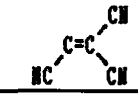
$R^1=R^2$	$R^3=R^4$	R^5	R^6	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	E_3^{Ox}	references
CH_3S	CH_3S	CH_3S	CH_3S	76		334 (20 420)$^{a)}$	0,55 0,1 M TEAP			63a
$COOCH_3$	$COOCH_3$	CHO	H		75					62
$-(CH=CH)_2-$	$-(CH=CH)_2-$	CHO	H		74					62
H	H		H		80		0,26 TBAP$^{e)}$	0,40	1,32	62

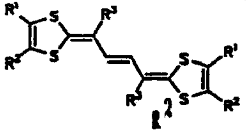
$COOCH_3$	$COOCH_3$		H	83		0,70 TBAP$^{e)}$	0,79	1,75	62
$-(CH=CH)_2-$	$-(CH=CH)_2-$		H	92	399$^{k)}$	0,50 TBAP$^{e)}$	0,62	1,53	62
$COOCH_3$	$COOCH_3$		CHO	86					62
$-(CH=CH)_2-$	$-(CH=CH)_2-$		CHO	85					62
H	H			80		0,25 TBAP$^{e)}$	0,37	0,72	62
$COOCH_3$	$COOCH_3$			89		0,73 TBAP$^{e)}$		1,14	62
$-(CH=CH)_2-$	$-(CH=CH)_2-$			73		0,54 TBAP$^{e)}$		0,97	62
$-(CH=CH)_2-$	$-(CH=CH)_2-$					0,49 0,1 M TBAHP$^{D)}$			228
$-(CH=CH)_2-$	$-(CH=CH)_2-$					0,56 0,1 M TBAHP$^{D)}$			228
H	H	C_6H_5	 $CH=C(CN)_2$	33					109

(*Continued*)

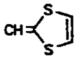
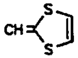
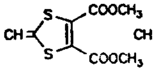
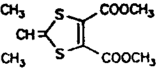
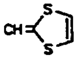
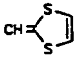
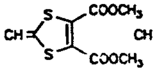
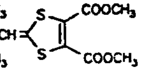
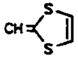
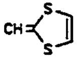
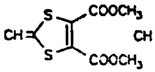
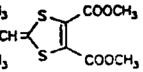
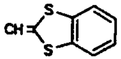
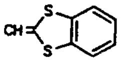
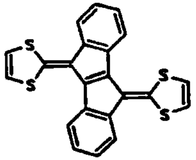
TABLE 7 (*Continued*)

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

$R^1=R^2$	$R^3=R^4$	R^5	R^6	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E^{Ox}_1	E^{Ox}_2 [V]	E^{Ox}_3	references
H	H	C_6H_5	 $(C_6H_5C{=}C)C{=}C(CN)_2$		77					109
H	H	C_6H_5	 $(C_2H_5OOC)C{=}C(CN)_2$		47					109
H	H	C_6H_5	 $(NC)C{=}C(CN)_2$		77	511 (27 540), 364 (22 400), 247 (25 700), 199 (51 300)$^{a)}$				109

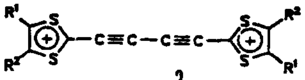


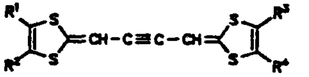
R^1	R^2	R^3	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E^{Ox}_1 [V]	E^{Ox}_2	references
H	H	$-CH_2CH_2-$	175-176 dec. (hexane)	68		0,23 0,1 M TEAP$^{g)}$		57
CH_3	CH_3	H	176-178 dec. (benzene)	52		0,21 0,1 M TEAP$^{g)}$		57

$\mathrm{C_6H_5}$	$\mathrm{C_6H_5}$	H	193-194 dec. ($\mathrm{CH_2Cl_2}$/hexane)	100		0,32 0,1 M TEAP$^{g)}$	57
$\mathrm{COOCH_3}$	$\mathrm{COOCH_3}$	$\mathrm{-CH_2CH_2-}$	202-204 (benzene/c-$\mathrm{C_6H_{12}}$)	94		0,57 0,1 M TEAP$^{g)}$	57
		H				0,12* 0,47* 0,1 M TBAP$^{q)}$	104
		H				0,27* 0,70* 0,1 M TBAP$^{q)}$	104
		$\mathrm{C_6H_5}$				0,25* 0,56* 0,1 M TBAP$^{q)}$	104
		$\mathrm{C_6H_5}$				0,30* 0,55* 0,1 M TBAP$^{q)}$	104
		p-$\mathrm{CH_3C_6H_4}$				0,20* 0,42* 0,1 M TBAP$^{q)}$	104
		p-$\mathrm{CH_3C_6H_4}$				0,30* 0,56* 0,1 M TBAP$^{q)}$	104
		p-$\mathrm{CH_3C_6H_4}$				0,25* 0,35* 0,1 M TBAP$^{q)}$	104
			260-262		518$^{a)}$	0,42 0,1 M TEAT	229

(*Continued*)

TABLE 7 (*Continued*)
Molecular properties of vinylogous, cumulenic, acetylenic, and quinoid TTF and TSF (redox potential in acetonitrile vs. sce)

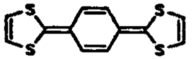
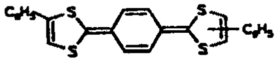
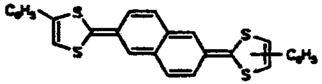
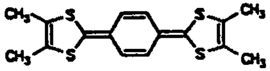
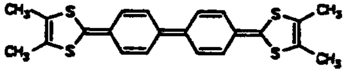
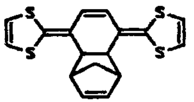
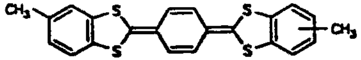
 R^1	R^2	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
CH_3	CH_3		87	465 (33 100), 431 (28 200), 388 sh (19 500)[j]	(- 0,12) 0,1 M TEAP[g]	(0,25)	67
C_6H_5	C_6H_5		74				67

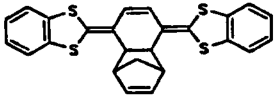
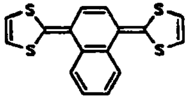
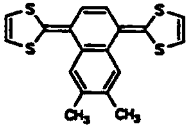
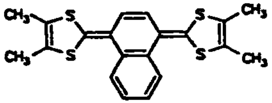
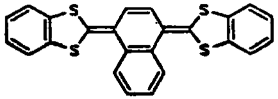
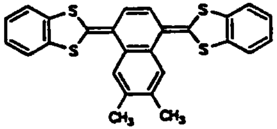
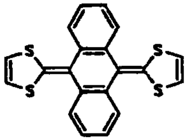
 R^1	R^2	R^3	R^4	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
H	H	H	H	98	23		(0,48) 0,1 M TBAP		64, 66
H	H	CH_3	CH_3	136-138	54		(0,47) 0,1 M TBAP		64, 66
CH_3	CH_3	CH_3	CH_3		20		(0,42) 0,1 M TBAP		64, 66
$-(CH_2)_3-$		$-(CH_2)_3-$					(0,41) 0,1 M TBAP		64, 66

$-(CH_2)_4-$		$-(CH_2)_4-$		216 dec.		(0,42) 0,1 M TBAP		64, 66
H	H	$COOCH_3$	$COOCH_3$		59	0,61 0,1 M TBAP	1,18	64, 66
CH_3	CH_3	$COOCH_3$	$COOCH_3$		54	0,54 0,1 M TBAP	1,18	64, 66
$-(CH_2)_3-$		$COOCH_3$	$COOCH_3$			0,54 0,1 M TBAP	1,14	64, 66
$-(CH_2)_4-$		$COOCH_3$	$COOCH_3$			0,54 0,1 M TBAP	1,13	64, 66
CH_3	CH_3	$-(CH=CH)_2-$		102				64, 66
$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	180	60	0,80 0,1 M TBAP	1,18	64, 66
$COOCH_3$	$COOCH_3$	$-(CH=CH)_2-$			74	0,72 0,1 M TBAP	1,18	64, 66
$-(CH=CH)_2-$		$-(CH=CH)_2-$			35	0,67 0,1 M TBAP	1,02	64, 66

(Continued)

TABLE 7 (*Continued*)
Molecular properties of vinylogous, cumulenic, acetylenic, and quinoid TTF and TSF (redox potential in acetonitrile vs. sce)

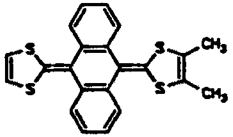
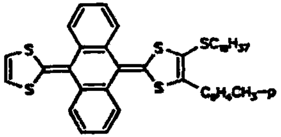
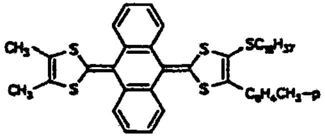
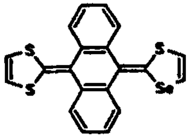
	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
	230-245 dec.	54	495 (60 200), 469 (31 600), 257 (11 750)$^{k)}$	- 0,11 0,1 M TEAP	- 0,04	75
				0,23		230
						231
						232
						233
				0,13 0,1 M TBAP$^{g)}$		69
	168-170 dec.	27	440 (44 650), 416 (38 000), 395 (20 400)$^{k)}$	0,17 0,1 M TEAP		75
						234

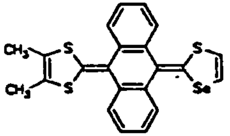
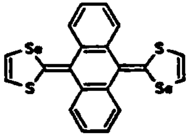
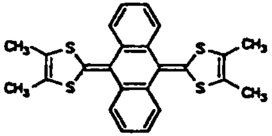
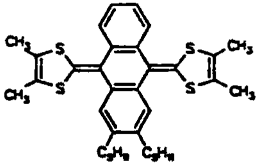
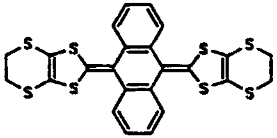
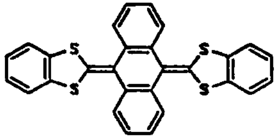
	260-265 dec.	73		0,37 0,1 M TEAP	75
	160-170 dec.			0,00 0,1 M TEAP	75
	190-194 dec.			- 0,04 0,1 M TEAP	75
				0,03 0,1 M TBAP$^{g,k)}$	235, 236
				0,06 0,1 M TBAP$^{g)}$	69
	260-270 dec.		468 (55 000)$^{k)}$	0,18 0,1 M TEAP	75
				0,40 0,1 M TBAP$^{k)}$	73
	243-248 dec.			0,15 0,1 M TEAP	75
	320-325 dec.	70	415, 323, 273, 253, 206$^{a)}$	0,40 0,1 M TBAP$^{g)}$	69, 235

(*Continued*)

TABLE 7 (*Continued*)

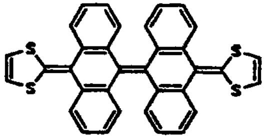
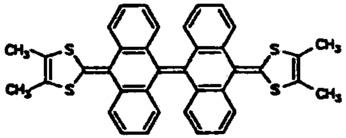
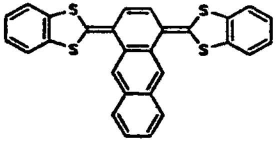
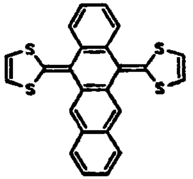
Molecular properties of vinylogous, cumulenic, acetylenic, and quinoid TTF and TSF (redox potential in acetonitrile vs. sce)

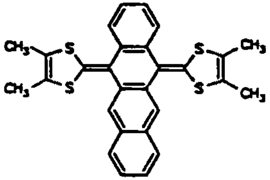
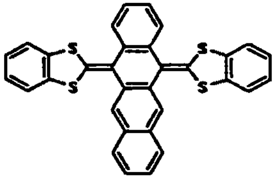
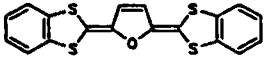
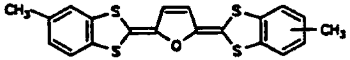
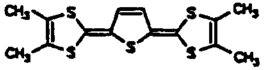
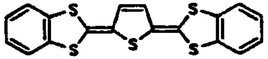
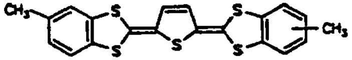
	m.p. [°C] (solvent)	yield [%]	λ_{max} (ε) [nm]	E_1^{0x} [V]	E_2^{0x}	references
				0,25 0,1 M TEAP		75
	> 260	74	430, 360, 235, 200[a]	0,36 0,1 M TBAP[g]		69, 77
	59	55		0,56 0,1 M TBAP[g]		77
	45	55		0,54 0,1 M TBAP[g]		77
	> 260	75	419, 365, 240[a]	0,47 0,1 M TBAP[g]		69, 77

	> 260	75	427, 363, 242a)	0,45 0,1 M TBAPg)	69, 77
 cis/trans mixture	> 240	63	409, 377, 265, 236a)	0,51 0,1 M TBAPg)	69
	> 230	75	433, 369, 235, 206a)	0,43 0,1 M TBAPg)	69, 235, 237
	199-202 (CH_2Cl_2/MeCN)	28		0,28	238
	196-197		440, 269, 238a)	0,48 0,1 M TBAPg)	70
	262-263 (EtOH)	73	415 (14 100), 398 (26 300), 348 (19 500), 237 (70 800)k)	0,39 0,1 M TBAPg)	58, 71, 239

(*Continued*)

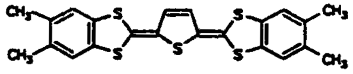
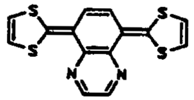
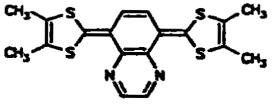
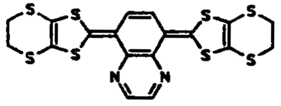
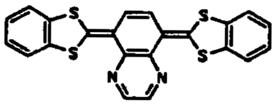
TABLE 7 (*Continued*)
Molecular properties of vinylogous, cumulenic, acetylenic, and quinoid TTF and TSF (redox potential in acetonitrile vs. sce)

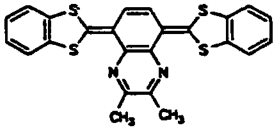
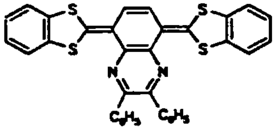
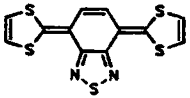
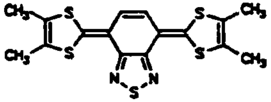
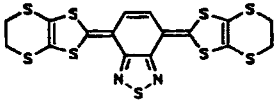
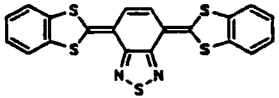
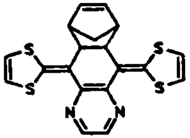
	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
	> 240	41	438, 378, 235, 200$^{a)}$	0,48 0,1 M TBAP$^{g)}$		69
	> 240	38	447, 381, 240, 200$^{a)}$	0,45 0,1 M TBAP$^{g)}$		69
	314-317 dec.			0,24 0,1 M TEAP		75
	> 240	59	417, 385, 235, 200$^{a)}$	0,44 0,1 M TBAP$^{g)}$		69

	> 240	55	428, 327, 230, 205$^{a)}$	0,41 0,1 M TBAP$^{g)}$		69
	285-290 dec.	48		0,39 0,1 M TBAP$^{g)}$		58
	218		478 (35 500)	- 0,21 0,1 M TBAHP$^{C,D)}$	0,07	228
	214		477 (39 800)	- 0,26 0,1 M TBAHP$^{C,D)}$	0,03	228
				0,09 0,1 M TBAP$^{k)}$	0,40	236
				0,04 0,1 M TBAP$^{k)}$	0,31	236
	> 300	70	476 (95 500), 453 (81 300)$^{c)}$	0,34 0,1 M TEAP$^{x)}$	0,58	241
				0,32 0,1 M TBAP$^{g)}$	0,57	58
	266-268		480 (48 900), 454 (42 600)$^{c)}$	0,30 0,1 M TEAP$^{x)}$	0,54	240, 241

(*Continued*)

TABLE 7 (*Continued*)
Molecular properties of vinylogous, cumulenic, acetylenic, and quinoid TTF and TSF (redox potential in acetonitrile vs. sce)

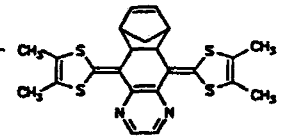
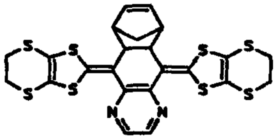
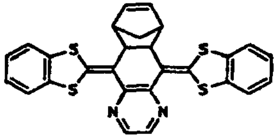
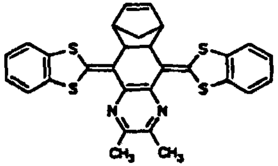
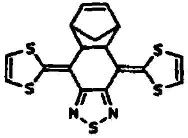
	m.p. [°C] (solvent)	yield [%]	λ_{max} (ε) [nm]	E_1^{Ox} [V]	E_2^{Ox}	references
	295-298		483 (22 400), 456 (19 500)$^{c)}$	0,28 0,1 M TEAP$^{x)}$	0,52	241
	279-280		504 (63 100), 475 (44 700)$^{k)}$	0,23 0,1 M TBAP$^{e)}$	0,43	74
	320 dec.		518 (64 600), 489 (44 700)$^{k)}$	0,17 0,1 M TBAP$^{e)}$	0,35	74
	265-267 dec.		522 (51 300), 490 (34 700)$^{k)}$	0,33 0,1 M TBAP$^{e)}$	0,49	74
	340-345	90	492 (33 100), 462 (24 000)$^{k)}$	0,37 0,1 M TBAP$^{k)}$	0,61	73
				0,44 0,1 M TBAP$^{e)}$	0,60	74

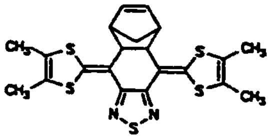
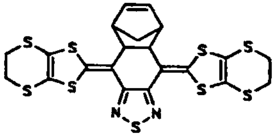
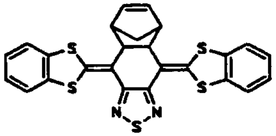
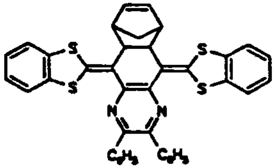
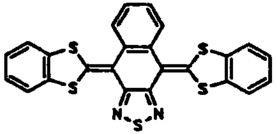
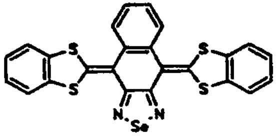
	315-318	90	489 (79 500), 462 (53 700)$^{k)}$	0,31 0,56 0,1 M TBAP$^{k)}$	73
	322-324	90	582 (5 880), 500 (69 200)$^{k)}$	0,44 0,67 0,1 M TBAP$^{k)}$	73
	297-298	95	494 (56 200), 464 (44 600)$^{k)}$	0,36 0,53 0,1 M TBAP$^{e)}$	242
	330 dec.	95	507 (56 200), 478 (44 600)$^{k)}$	0,30 0,48 0,1 M TBAP$^{e)}$	242
	> 400	95	511 (50 100), 480 (37 100)$^{k)}$	0,45 0,60 0,1 M TBAP$^{e)}$	242
	409-410	95	482, 454$^{k)}$	0,54 0,70 0,1 M TBAP$^{e)}$	242
		8			74

(*Continued*)

TABLE 7 (*Continued*)

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

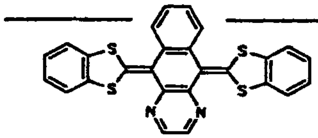
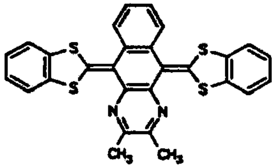
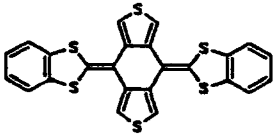
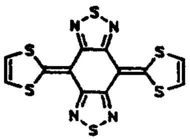
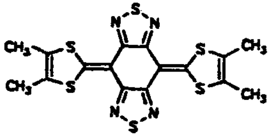
	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
		41				74
		50				74
		58	394 (51 300)$^{k)}$			73
		80	389 (45 700)$^{k)}$			73
		22				242

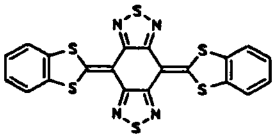
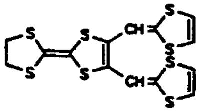
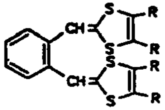
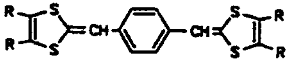
		72				242
		75				242
		92				242
		54	490 (15 130), 428 (32 350)k)	0,82 0,1 M TBAPk)	0,94	73
	367-370	90	422 (43 600), 360 (16 200), 235 (38 000)k)	0,65 0,1 M TEAP		71
	345-347	69	414 (39 800), 305 (15 500), 233 (37 200)k)	0,70 0,1 M TEAP		71

(*Continued*)

TABLE 7 (*Continued*)

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

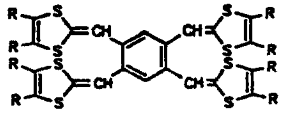
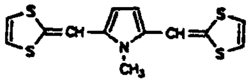
	m.p. [°C] (solvent)	yield [%]	λ_{max} (ε) [nm]	E_1^{Ox} [V]	E_2^{Ox}	references
	273-274	4	438 (41 700), 370 (15 130)$^{k)}$	0,66 0,1 M TBAP$^{k)}$		73
	270-272	8	439 (45 700), 365 (15 130)$^{k)}$	0,61 0,1 M TBAP$^{k)}$		73
	376-378	38	374 (38 900), 335 (22 900) 248 (39 800)$^{k)}$	0,78$^{k)}$		71
	> 450	48	542 sh, 470$^{B)}$			72
	> 400					72

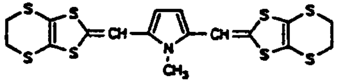
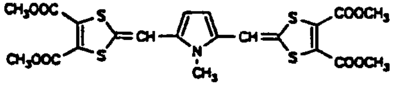
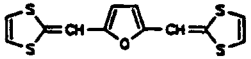
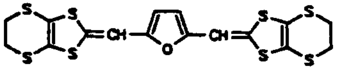
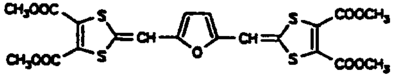
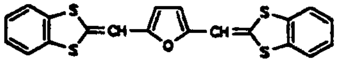
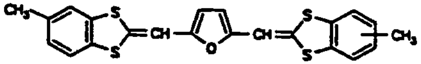
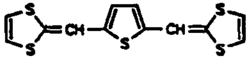
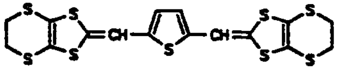
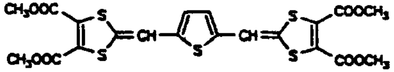
		> 400	50	420, 400, 380, 302, 257, 240[k)]		71
			70		0,22 0,30 0,1 M TBAP[q)]	102
	R $-(CH=CH)_2-$	175 ($CHCl_3$/ hexane)	75		$(0,85)^*$ $(0,95)^*$ 0,1 M TBAP[q)]	68
					$(0,93)^*$ $(1,05)^*$ 0,1 M TBAP[v)]	68
	$COOCH_3$		90		$(1,04)^*$ 0,1 M TBAP[q)]	68
					$(1,20)^*$ 0,1 M TBAP[v)]	68
	R $-(CH=CH)_2-$	292-294 (DMF)		409 (50 100), 390 (56 200)	0,78 0,1 M TBAP[q)]	58
		291 dec.	40		$(0,72)^*$ $(0,86)^*$ 0,1 M TBAP[q)]	68
	$COOCH_3$				$(0,88)^*$ $(1,08)^*$ 0,1 M TBAP[q)]	68
					$(1,03)^*$ 0,1 M TBAP[v)]	68

(*Continued*)

TABLE 7 (*Continued*)

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

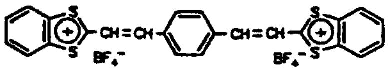
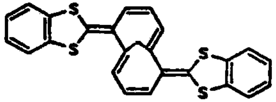
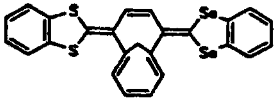
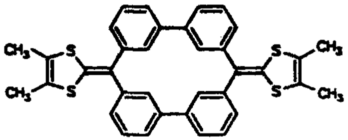
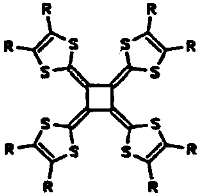
		m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
	R H	159 dec. (PhCl)	59		(0,46)* 0,1 M TBAP$^{q)}$		68
					0,54 0,1 M TBAP$^{v)}$	0,66	68
	-(CH=CH)$_2$-	> 260 (PhCl)	90		(0,68)* 0,1 M TBAP$^{q)}$		68
					(0,68)* 0,1 M TBAP$^{v)}$	(0,96)*	68
	COOCH$_3$	221-226	50		(0,85)* 0,1 M TBAP$^{q)}$	(0,99)*	68
					(0,96)* 0,1 M TBAP$^{v)}$	(1,15)*	68
		148-149	8		0,20 0,1 M TBAHP	0,38	243

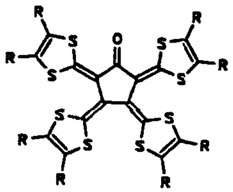
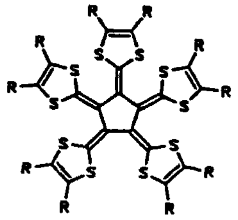
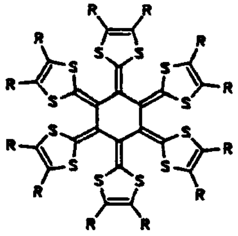
	199-200 (CH_2Cl_2)	87		0,31 0,1 M TBAHP$^{k)}$	0,58	243
	188	88		0,48 0,1 M TBAHP	0,71	243
	122-124	23		0,32 0,1 M TBAHP		243
	213-214 ($CHCl_3$)	66		0,38 0,1 M TBAHP$^{k)}$	0,56	243
	89	99		0,58 0,1 M TBAHP	0,71	243
	174		400 (40 750)	0,01 0,1 M TBAHP$^{C,D)}$	0,14	228
	168		404 (35 500)	- 0,04 0,1 M TBAHP$^{C,D)}$	0,10	228
	133-134	43		0,39 0,1 M TBAHP	0,49	224
	230-231 (toluene)	51		0,46 0,1 M TBAHP$^{k)}$	0,65	224
	149	91		0,69 0,1 M TBAHP	0,79	224

(*Continued*)

TABLE 7 (*Continued*)

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

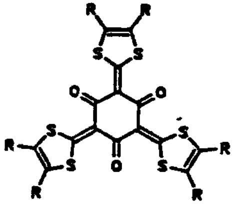
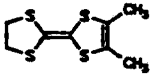
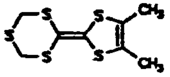
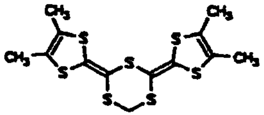
		m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox} [V]	references
		> 340	64		0,40 0,1 M TBAP$^{g)}$		58
		> 220 dec.	99	490 (9 550), 310 (2 000), 262 (5 130), 239 (13 800)$^{k)}$	0,44 0,1 M TBAHP$^{g)}$		244
		275-276 dec.	99	451 (38 000), 338 (9 330), 317 (8 320), 242 (38 000)$^{k)}$			76
		271	61		0,91 0,1 M TBAP$^{k,z)}$	1,33	245
	R						
	H	170 dec. (benzene)			0,19 (1,30)	(0,98)	230, 246
	-(CH=CH)$_2$-				0,43	0,72	230
	COOCH$_3$	235-238 (benzene/hexane)			0,65	0,70	246

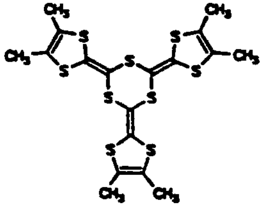
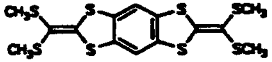
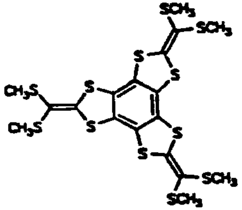
	R H		250 dec.	88		0,17	$1,14^{e,g)}$	61
	-(CH=CH)$_2$-		298	84		0,38	$1,22^{e,g)}$	61
	COOCH$_3$		292	77		0,64	$1,35^{e,g)}$	61
	R -(CH=CH)$_2$-					$0,36^{e,g)}$		59
 a boat–conformation b chair–conformation	R -(CH=CH)$_2$-	a	> 300	72	393 (17 000), 338 (35 500)$^{l)}$	0,43 (0,81) 0,1 M TBAP$^{e,g)}$	(0,65)	60
		b	> 300		354 (46 700)$^{l)}$	0,82 0,1 M TBAP$^{e,g)}$		60
	COOCH$_3$	a	> 300	35	386 (31 600), 331 (61 600)$^{k)}$	0,73 (1,13) 0,1 M TBAP$^{g,k)}$	(0,89)	60
		b	> 300		354 (44 600), 286 (36 300)$^{k)}$	1,14 0,1 M TBAP$^{g,k)}$		60

(*Continued*)

TABLE 7 (*Continued*)

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

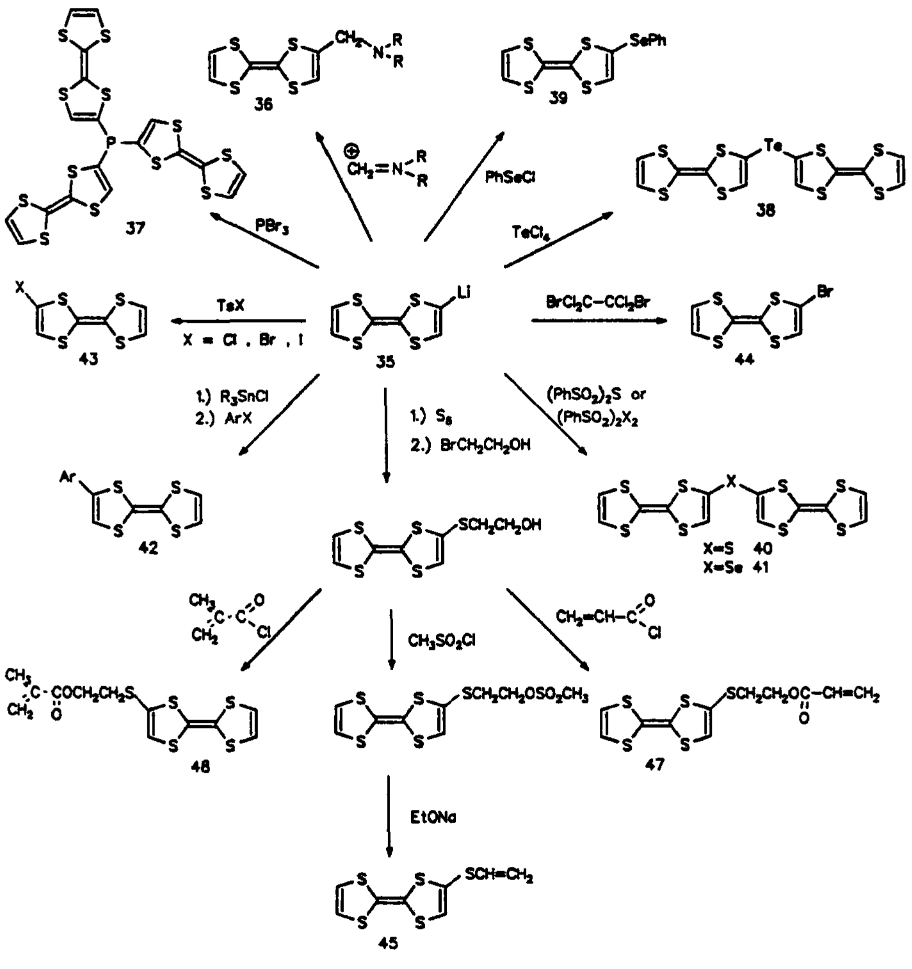
		m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
	R Pr	312-315 (EtOH)	30		0,65 (1,25) 0,1 M TBAHP$^{g,x)}$	0,80	247
		140 (EtOAc/hexane)	57	367 (1 950), 328 (11 750), 318 (10 700), 268 (3 540)$^{w)}$	0,75 0,1 M TBAHP$^{n)}$	1,13	135
		168 (hexane)	68	355 (6 025), 330 (13 500), 318 (10 000), 260 (4 070)$^{w)}$	0,75 0,1 M TBAHP$^{n)}$	1,13	135
		203 (acetone/hexane)	30	363 (14 130), 334 (24 550), 322 (21 850), 264 (9 130)$^{w)}$	0,60 0,1 M TBAHP$^{n)}$		135

	216 (CS_2)	25	367 (12 900), 334 (18 200), 256 (7 420)$^{w)}$	0,59 0,68 0,1 M TBAHP$^{n)}$	0,82	135
		20		0,77 TBAHP$^{k)}$	1,0	248
				0,93 1,51 TBAHP$^{k)}$	1,16	248

6. PROPERTIES OF TETRACHALCOGENAFULVALENES

6.1 *Reactions of Tetrathia- and Tetraselenafulvalenes*

Metallation of TTF with different lithiation agents (LDA—lithium diisopropylamide, LiHMDS—lithium hexamethyldisilazane, PhLi, MeLi, BuLi) provides tetrathiafulvalenyllithium **35** as a reactive intermediate.[78] By treatment with electrophiles monosubstituted TTF can be synthesized.



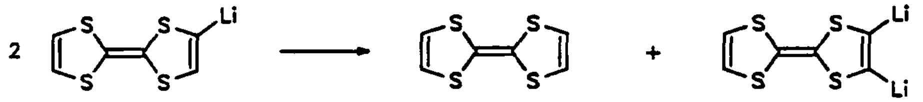
The first *N,N*-dialkylaminomethyl substituted TTF **36** were obtained in yields of 35–50% by reaction of tetrathiafulvalenyllithium **35** with Eschenmoser's salts.[79] The best yields were obtained with LDA as the metallation agent. The metallated TTF **35** with the halides PBr_3 or $TeCl_4$ provides the corresponding trimers

$P(TTF)_3$ **37**[80] or dimers $Te(TTF)_2$ **38**[81,82] (yield 40% and 20%, respectively). With benzeneselenenyl chloride the phenylseleno-TTF **39** is formed. 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.[83]

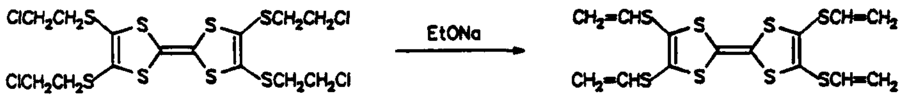
Reaction of the monoanion **35** with di(phenylsulfonyl) sulfide, di(phenylsulfonyl) disulfide, or di(phenylsulfonyl) diselenide produces the corresponding sulfur or selenium bridged dimer bis(tetrathiafulvalenyl) sulfide **40** or bis(tetrathiafulvalenyl) selenide **41** in moderate yields.[84]

After conversion of tetrathiafulvalenyllithium **35** to the corresponding trialkylstannyl derivative with trialkylstannyl chloride, an aryl substituted TTF **42** or bitetrathiafulvalene can be prepared by palladium catalysed coupling reaction with aryl halides.[85] Halogenation of the lithiated species (lithiated by LDA) with the appropriate *p*-toluenesulfonyl halide affords the monohalogenated TTF derivatives **43** in good yields (35–50%).[86] The yield of bromotetrathiafulvalene **44** is decreased when 1,2-dibromotetrachloroethane is used as halogenating agent.[87]

Similarly, in all reactions of tetrathiafulvalenyllithium **35** with electrophiles the disubstituted derivative is formed as a by-product. This is probably due to the tendency of tetrathiafulvalenyllithium to undergo disproportionation.[78] The yield of the by-product depends on the metallation agent.[87]

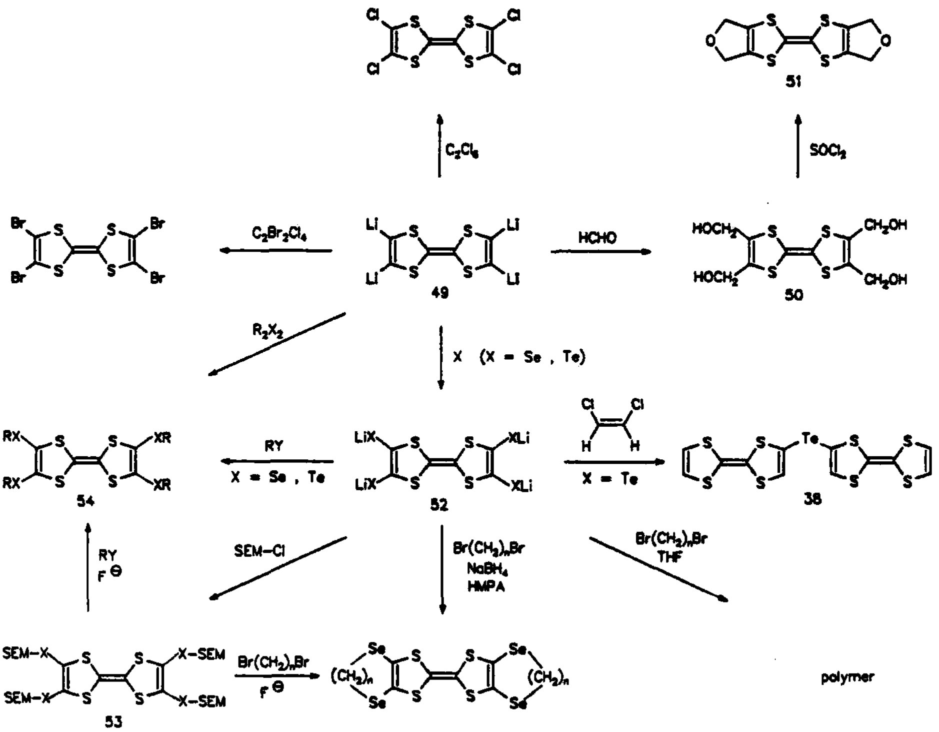


Reaction of monolithio-TTF **35** with elemental sulfur provides the thiolate anion, which can be alkylated with 2-bromoethanol. A following mesylation and treatment with sodium ethoxide gives vinylthio-TTF **45**.[88] In an analogous manner the base-induced elimination of hydrogen chloride from tetrakis(chloroethylthio)tetrathiafulvalene affords tetra(vinylthio)tetrathiafulvalene **46**. Hydroxyethylthio-TTF can be converted with acryloyl or methacryloyl chloride under basic conditions to the acrylate **47** or methacrylate derivative **48**, respectively.



46

Tetralithiated TTF **49**[89] has been chlorinated or brominated with hexachloroethane or 1,2-dibromotetrachloroethane, respectively (yield 15%). When iodine was used as the halogenating agent the desired product was not obtained.[90] TTF-

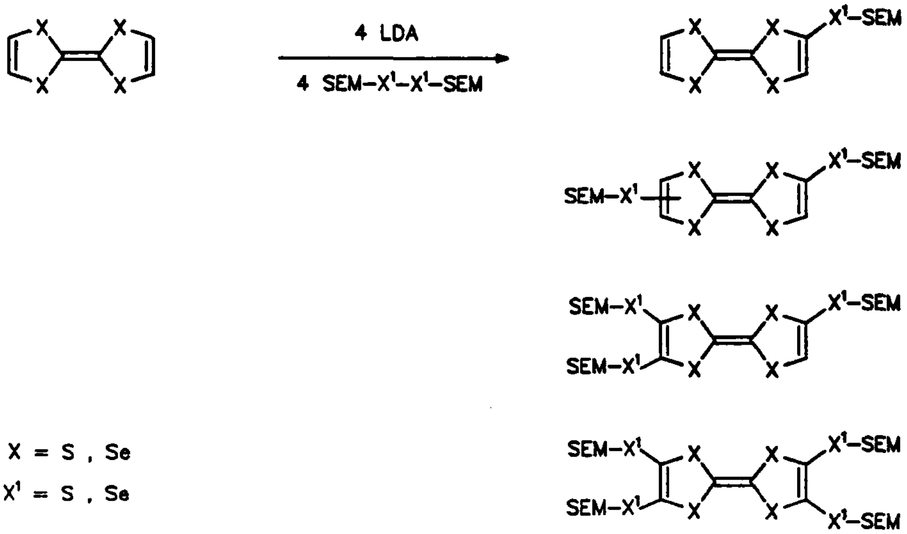


tetratellurolate anion reacts with *cis*-dichloroethylene. The unsaturated telluro analog of bis(ethylenedithio)-TTF is not obtained, but bis(tetrathiafulvalenyl) telluride **38** is formed in 20% yield.[81]

The intermediate tetralithio-TTF **49** reacts with formaldehyde and provides tetrakis(hydroxymethyl)-TTF **50** which can be converted with thionyl chloride to bis(oxydimethylene)-TTF **51**.[91] The tetralithiation of TTF and subsequent chalcogen insertion into the carbon-lithium bonds of tetralithio-TTF provides the TTF-tetrachalcogenolate anion **52**. Attempts at intramolecular alkylative ring closure of selenium and tellurium derivatives with dibromoalkanes only lead to polymeric products. Obviously, these are formed by predominantly intermolecular alkylation, even with high dilution or at lower temperatures.[92] In order to solve this problem, the TTF-tetrachalcogenolate anions **52** have been converted to a stable intermediate by reaction with 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 agents alkylseleno-TTF are obtained in good yields (30–35%).

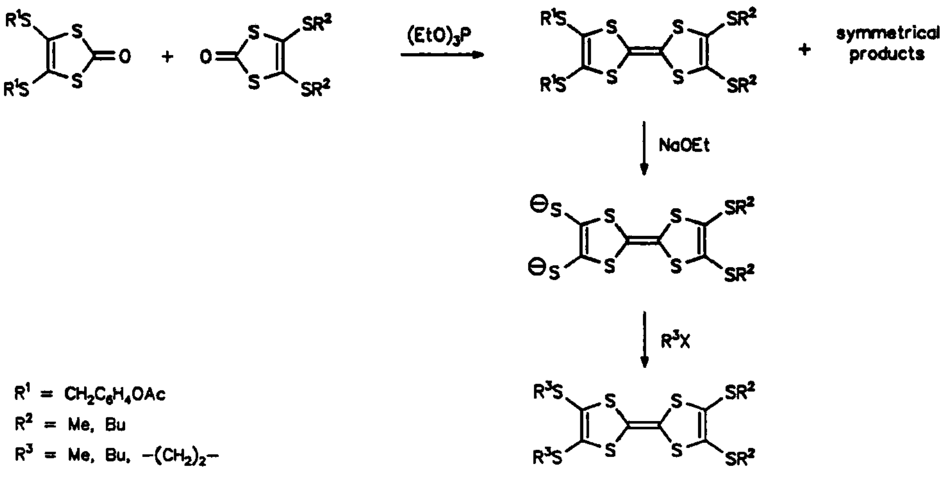
In the case of the TTF-tetratellurolate anion tetrakis(SEM-telluro)-TTF **53** (X = Te) is produced in good yield (63%), but reaction with dibromoalkanes in the presence of tetrabutylammonium fluoride fails to provide the desired products.[92] The formation of polymers in the reaction of TTF-tetraselenolate anions **52** (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 the solvent THF by hexamethylphosphoramide (HMPA) a dipolar aprotic solvent, allows the bis(alkylseleno)-TTF 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.[93]

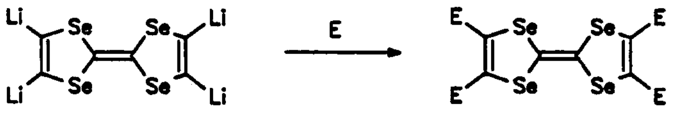
Reaction of the TTF-tetrachalcogenolate anions **52** as well as reaction of tetrakis(SEM-chalcogeno)-TTF **53** after removal of the protecting group with tetrabutylammonium fluoride with alkyl halides yields the tetrakis(alkylchalcogeno)-TTF **54**.[87,94–96] Via an alternative route the tetrakis(alkylchalcogeno)-TTF **54** (X = S, Se) can also be prepared in good to excellent yields (64–90%): by reaction of tetralithio-TTF **49** with various dialkyl or diaryl disulfides or diselenides as electrophiles.[97] The same reaction opened up the possibility of synthesis of unsymmetrically 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%.[98] This product mixture



is 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.

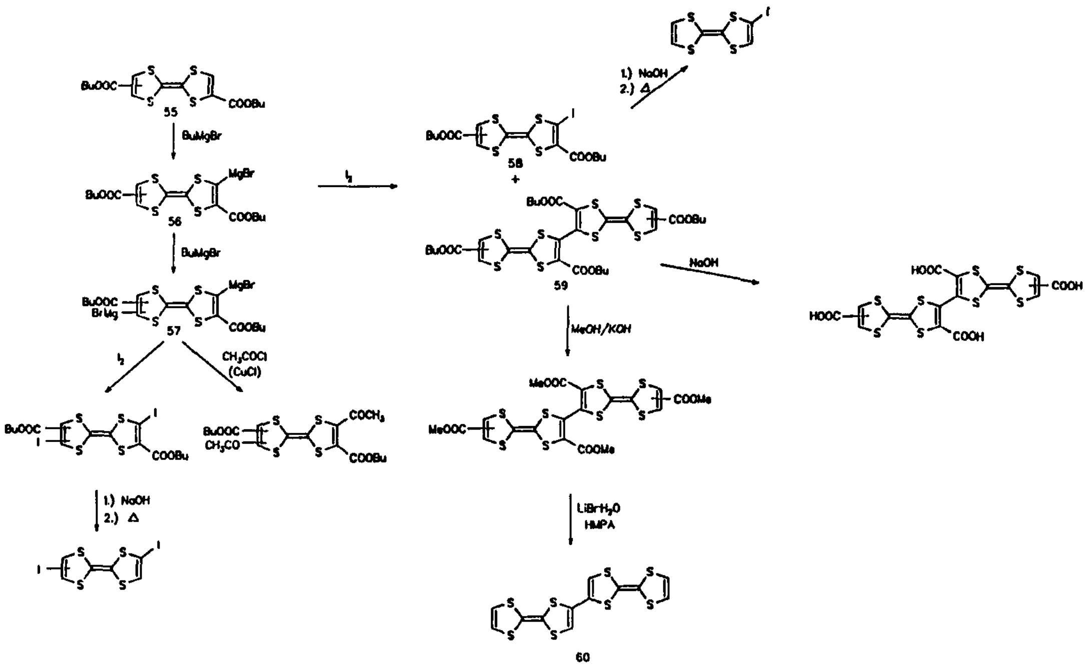
Unsymmetrical TTF have also been synthesized with the 4-acetoxybenzyl group as a blocking group.[98a] After cross-coupling of two 1,3-dithiol-2-ones the resulting product mixture is separated by flash column chromatography. The protecting group is then removed with sodium ethoxide in ethanol or sodium *tert.*-butylthiolate in tetrahydrofuran at −10 °C. The dithiolate thus formed is then quenched with alkyl halides. TSF also can be converted with LDA to the tetralithio derivative. Treatment of TSF with *n*-butyllithium under conditions employed with TTF led to total destruction of the TSF framework.[99] Reaction of tetralithio-TSF with excess 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%).[96,99,100]



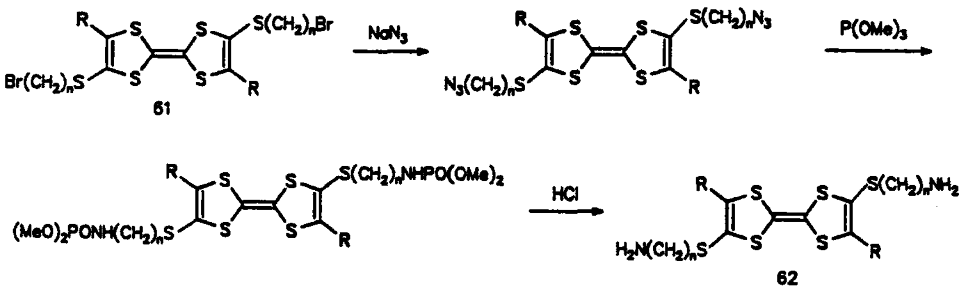


Metallation of TTF derivatives can also be achieved by reaction with Grignard agents.[101] Treatment of bis(butoxycarbonyl)-TTF **55** with butylmagnesium bromide gives the monometallated derivative **56**, further reaction with butylmagnesium bromide the dimetallated derivative **57**. Both react easily with electrophiles, e.g. acetyl chloride, 2-chloroethyl formate or iodine and provide the corresponding derivatives (Scheme 3).

In the reaction of bis(butoxycarbonyl)tetrathiafulvalenyl-magnesium bromide **56** with iodine a mixture of two products is formed, a monoiodo substituted TTF **58** (37%) and a dimerized TTF derivative **59** (25%). The butoxycarbonyl group in the TTF derivatives can be hydrolyzed in refluxing alkaline mixture of water and dioxan. Upon heating in diglyme the acid decarboxylates. With methanol in alkaline solution the butoxycarbonyl group is converted to a methoxycarbonyl group.



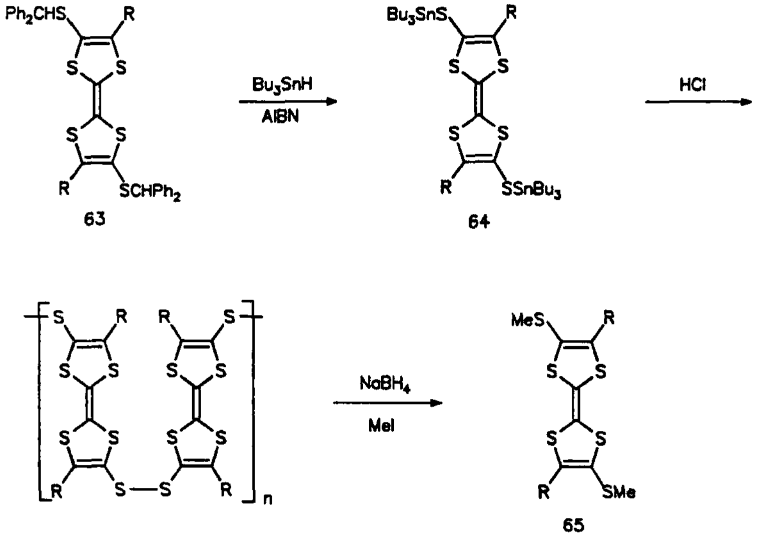
Demethoxycarbonylation with lithium bromide monohydrate at 150 °C provides the unsubstituted dimerized TTF **60**. The synthetic route to TTF via mesoionic 1,3-dithioles made it possible to prepare many substituted TTF derivatives which in turn can be converted to new derivatives.[31] Thus the bis(aminoalkylthio)-TTF **62** (n = 3,6) are obtained by nucleophilic substitution of the bis(bromoalkylthio)-TTF **61** with sodium azide in DMSO, followed by treatment with trimethyl phosphite and subsequent hydrolysis with hydrochloric acid.


61

62

R = $CH_3(CH_2)_{10}$, p-MeC_6H_4 , p-ClC_6H_4

In a radical initiated reaction the bis(benzhydrylthio)-TTF **63** are treated with tributylstannane and provide the bis(tributylstannylthio)-TTF **64**. Further reaction with gaseous hydrogen chloride leads to S-S bond formation and formation


63

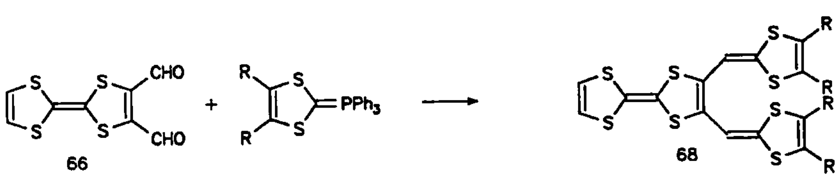
64

65

R = $CH_3(CH_2)_{10}$, p-MeC_6H_4 , p-ClC_6H_4

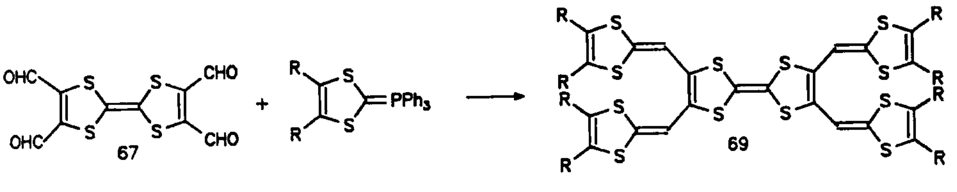
of polymeric TTF. The S-S linkages of polymeric TTF can be cleaved with sodium borohydride and alkylated with methyl iodide to form bis(methylthio)-TTF **65**.[31]

An aldehyde functional group of TTF is very reactive and upon treatment with a phosphorane forms an olefinic bond. Wittig reaction of the 1,2-diformyl-TTF **66** and the tetraformyl-TTF **67** with phosphoranes produces the bis- and tetrakis(1,4-dithiafulvenyl)-TTF **68** and **69** in yields of 70–80%.[102] Treatment of



66

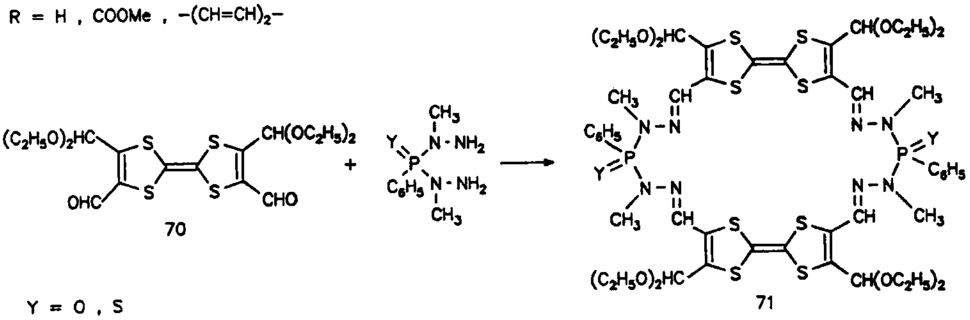
68



67

69

R = H , COOMe , $-(CH=CH)_2-$

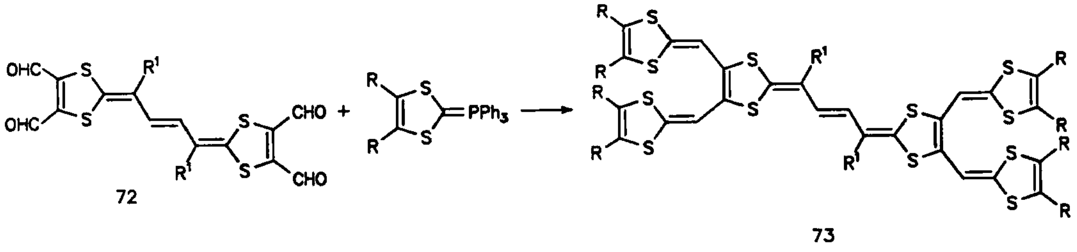


70

71

Y = O , S

phosphodihydrazides (Y = O, S) with the cis isomer of the diacetalized tetraformyl-TTF **70** leads to the macrocycles **71** in yields of 80% and 60% respectively.[103]

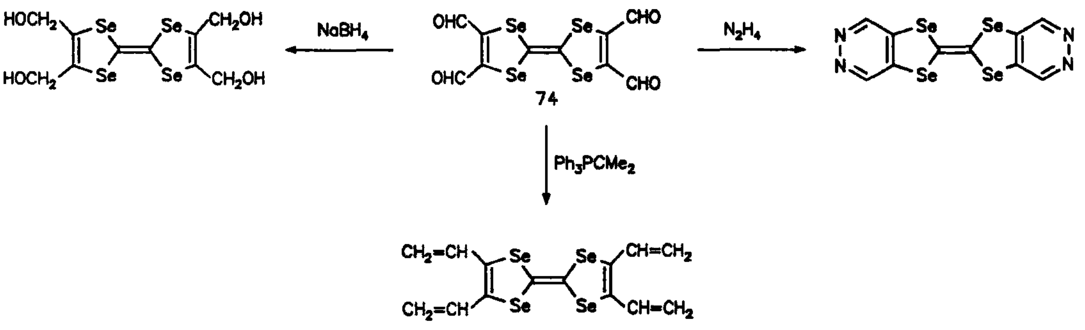


72

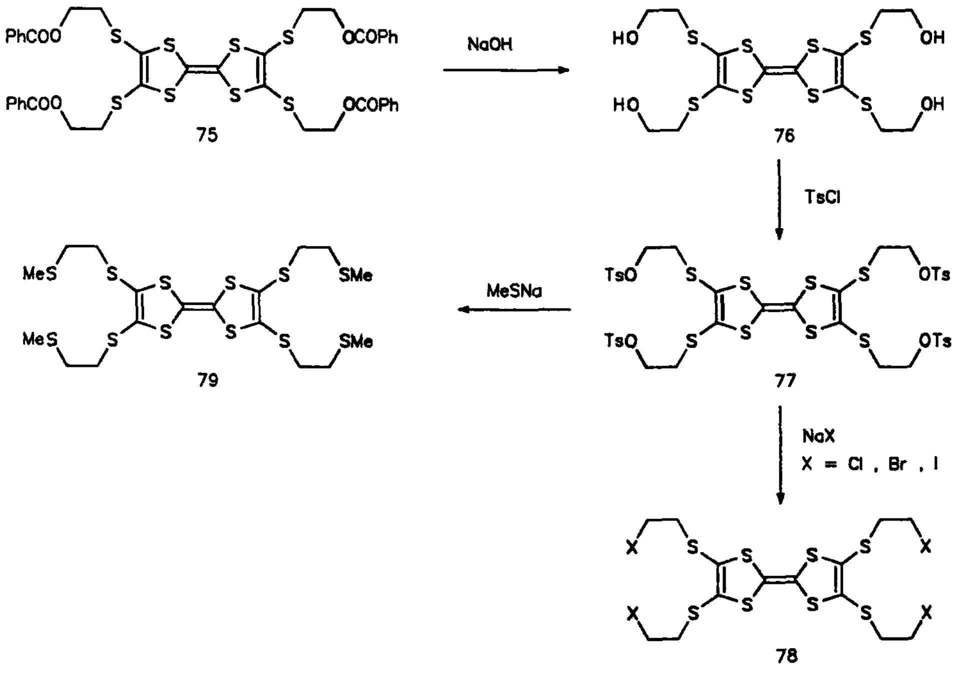
73

R = H , COOMe , $-(CH=CH)_2-$
R^1 = H , Ph , $p-MeC_6H_4$

Also tetraformyl vinylogs of TTF **72** react with phosphoranes or phosphonate anions to TTF derivatives **73** with a more extended π-system.[104] The tetraformyl-TSF **74** is an efficient precursor of heteroannellated and tetrasubstituted TSF.[52]

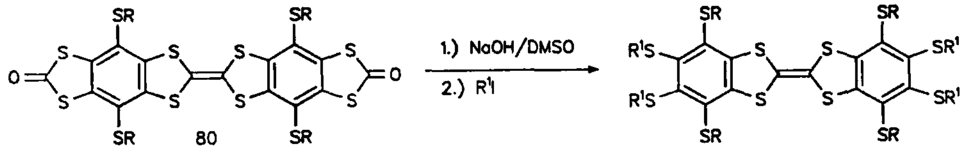


The TTF framework is stable towards nucleophilic agents so that substituents can be modified in nucleophilic reactions without loss of the TTF moiety.[105,106] Hydrolysis of the tetrakis-(benzoyloxyethylthio)-TTF **75** takes place in alkaline



solution to form the tetrakis(hydroxyethylthio)-TTF **76**. This compound reacts with tosyl chloride to the corresponding tosylate **77** which can be further converted with sodium methanethiolate to the tetrakis(haloethylthio)-TTF **78** or tetrakis(methylthioethylthio)-TTF **79**, respectively, in almost quantitative yield.

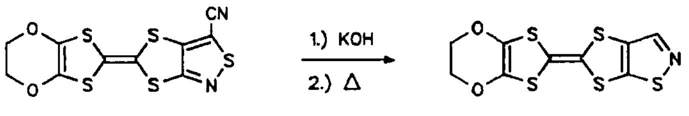
Sodium hydroxide in DMSO hydrolyzes the 1,3-dithiol-2-one system also in the benzo annelated TTF **80**.[107] The tetrathiolate formed can be alkylated with alkyl iodides.



80

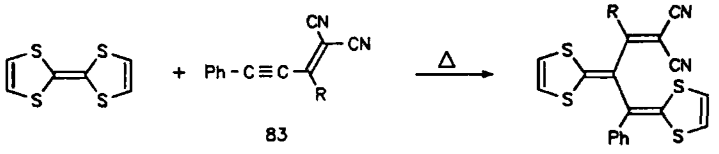
R = Me, n-Pent
R' = Me , $-CH_2-$

Refluxing of the thiazoloethylendioxo-TTF **81** in alkaline solution, followed by heating of the acid in DMF with decarboxylation and simultaneous rearrangement, provides the isothiazoloethylenedioxo-TTF **82**.[108] The dicyano(ethynyl)-



81 82

ethenes **83** and TTF do not form charge transfer complexes but new covalent compounds.[109] 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.

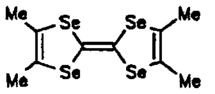


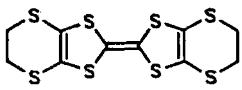
83

R = H , COOEt , CN , Ph-C≡C

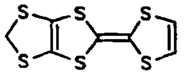
6.2. *Organic Superconductors*

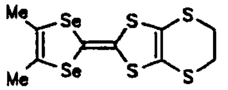
After the discovery of ambient pressure superconductivity in the tetramethyltetraselenafulvalenium salt $(TMTSF)_2ClO_4$ and the bis-(ethylenedithio)tetrathiafulvalenium salt $(\mathrm{BEDT\text{-}TTF})_2\mathrm{I}_3$ many charge-transfer complexes with tetrachalcogenafulvalenes as donors have been prepared in the hope of finding new organic conductors or even superconductors.

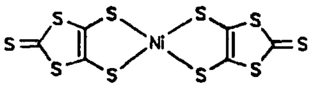

TMTSF

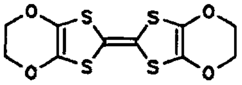

BEDT-TTF

In the meantime superconductivity has been observed in a complex with the unsymmetrically substituted TTF derivative MDT-TTF, in complexes with the DSDTF derivative DMET and in a complex with $\mathrm{Ni(dmit)_2}$ as acceptor (Table 2).


MDT-TTF


DMET


$\mathrm{Ni(dmit)_2}$


BEDO-TTF

However, the highest temperature T_c for the transition of an organic conductor to an organic superconductor is observed with BEDT-TTF salts (Table 2). Also in a complex with the oxygen-containing donor BEDO-TTF superconductivity at ambient pressure has been found.

7. SYNTHESIS AND PROPERTIES OF POLYMERIC TETRATHIAFULVALENES

A polymer backbone with attached tetrathiafulvalene units has been prepared by reaction of poly[*p*-(chloromethyl)styrene] **84** or poly-[styrene-co-*p*-(chloromethyl)styrene] **85** with potassium 4-tetrathiafulvalenylphenoxide. The polymers **86** and **87** with a variety of controlled molecular weights and molecular weight distributions differ in their solubility. Whereas polymers **86** are highly insoluble, the polymers **87** are soluble in dichloromethane.[128] The suitability of the polymers **86** and **87** for microlithographic processes is being studied.

TABLE 2

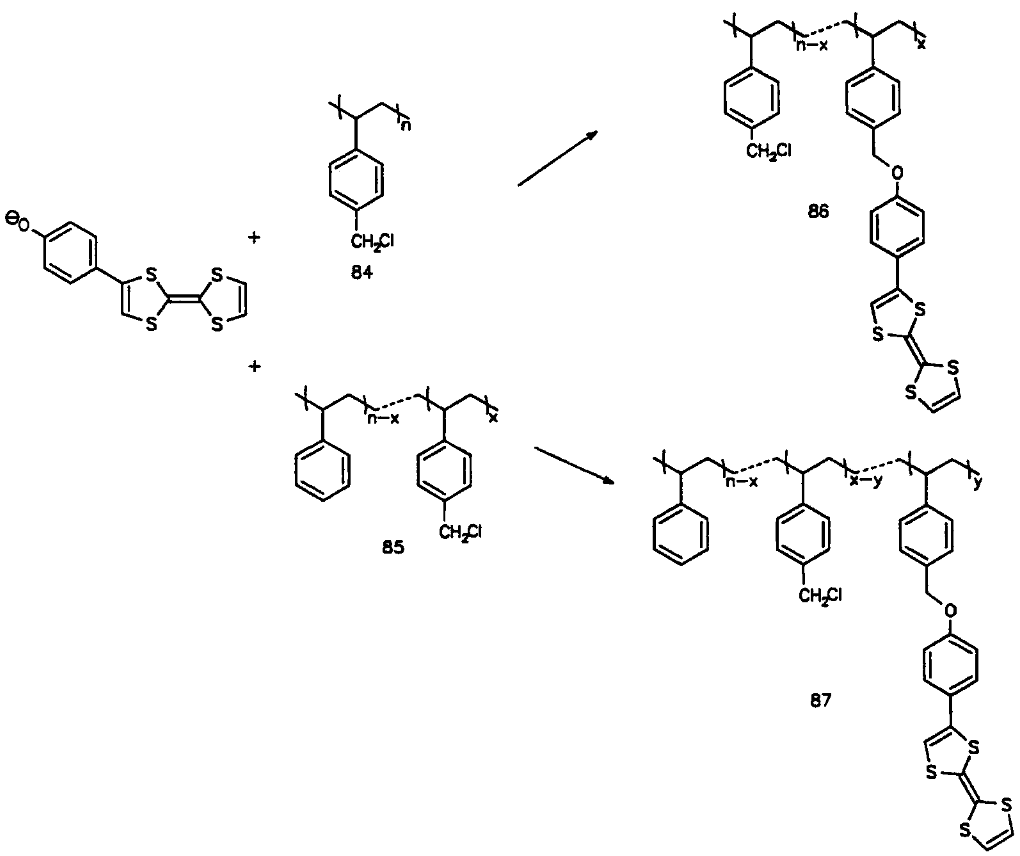
Organic superconductors and their transition temperature T_c to superconductivity

Complex	T_c* [K]	references
$(TMTSF)_2\ ClO_4$	1,4	110
$(MDT\text{-}TTF)_2\ AuI_2$	3,5	111
$(DMET)_2\ AuCl_2$	0,83	112
$TTF[Ni(dmit)_2]_2$	1,6 (7 kbar)	113
$(BEDT\text{-}TTF)_2\ ReO_4$	2 (4 kbar)	114
$(BEDT\text{-}TTF)_2\ I_3$	1,5	115
	8 (1,3 kbar)	116
$(BEDT\text{-}TTF)_2\ IBr_2$	2,5	117
$(BEDT\text{-}TTF)_2\ AuI_2$	3,8 - 5	118
$(BEDT\text{-}TTF)_2\ (I_3)_{2,5}$	2,5	119
$(BEDT\text{-}TTF)_4\ Hg_3Cl_8$	1,8 (12 kbar)	120
$(BEDT\text{-}TTF)_4\ Hg_3Br_8$	4,3	121
$(BEDT\text{-}TTF)_3\ Cl_2(H_2O)_2$	2 (16 kbar)	122
$(BEDT\text{-}TTF)_4\ Pt(CN)_4H_2O$	2	123
$(BEDT\text{-}TTF)_2\ Cu(NCS)_2$	10,4	124
$(BEDT\text{-}TTF)_2\ Cu[N(CN)_2]Br$	12,5	125
$(BEDT\text{-}TTF)_2\ Cu[N(CN)_2]Cl$	12,5 (0,3 kbar)	126
$(BEDO\text{-}TTF)_3\ Cu_2(NCS)_3$	1,06	127

* Unless otherwise noted, T_c is at ambient pressure.

Deprotonation of the corresponding bis-1,3-dithiolium salt provides the planar and conjugatively connected polytetrathiafulvalene **88**. This polymer reacts with bromine, iodine or TCNQ and forms radical cation salts with an electrical conductivity of up to $3 \cdot 10^{-4}$ $S \cdot cm^{-1}$.[129] The radical cation salts of **88** show a higher conductivity than twisted phenylene-bridged polymeric radical cation salts.[129–131]

The oxidation of the polymer **88** by bromine or iodine leads to the generation of charge carriers (polarons, bipolarons) which are responsible for the conductivity.[132,133] A polymer with tetrathiafulvalene units bridged by S-S linkages is formed by treatment of bis(tributylstannylthio)-TTF **64** with gaseous hydrogen chloride (see Chapter 6.1.).[31]

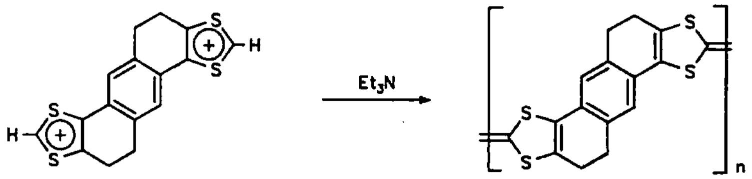


84

85

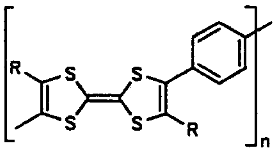
86

87



88

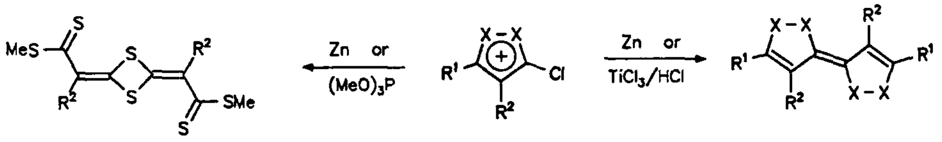
R = H, Me, Et



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

1,2-TTF are synthesized by reduction of 1,2-dithiolium salts with activated zinc or $TiCl_3$/HCl in acetonitrile. The yield in the reduction with activated zinc is increased by supersonication.

Dimerization of 5-methylthio substituted 1,2-dithiolium salts with activated zinc or trimethyl phosphite gives the 1,3-dithietanediylidene-bis(methyldithioacetate) derivatives **89**.[134] Diphenyl substituted 1,2-tetraselenafulvalenes are obtained in low yield (5%) by reduction of the corresponding 1,2-diselenolium salts with activated zinc.[134] 1,2-TTF and 1,2-TSF and their data are summarized in Table 8.



89

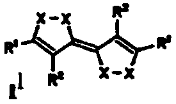
X = S
R¹ = MeS
R² = MeS, Ph, p−MeC₆H₄

X = S
R¹ = Ph
R² = MeS, Ph

X = Se
R¹ = R² = Ph

TABLE 8

Molecular properties of 1,2-TTF and 1,2-TSF (redox potential in acetonitrile vs. sce)



R^1	R^2	X	m.p. [°C] (solvent)	yield [%]	λ_{max} [nm] (ε)	E_1^{Ox} [V]	E_2^{Ox}	references
C_6H_5	C_6H_5	S	290	52	500 (12 600)^{w}	0,21	0,43	134
C_6H_5	CH_3S	S	208	16	550 (7 950)^{w}	0,30	0,52	134
C_6H_5	C_6H_5	Se	304	5	497 (15 800), 338 (63 000)^{w}			134

a) in acetonitrile, b) in hexane, c) in tetrahydrofurane, d) in cyclohexane, e) in benzonitrile, f) in methanol/benzene (4:1,v:v), g) vs. Ag/AgCl electrode, h) vs. $Ag/AgNO_3$ (0,01M) electrode, i) probably trans-isomer, j) 70 % perchloric acid, k) in methylene chloride, l) in benzene, m) in chlorobenzene, n) in 1,2-dichloroethane, o) in 0,1 N resp. 0,01 N sodium hydroxide, p) in ethanol, q) in N,N-dimethylformamide, r) in isooctane, s) in methanol, t) in dioxan , u) in carbon disulfide, v) in 1,1,2-trichloroethane, w) in chloroforme, x) in propionitrile, y) in butyronitrile, z) vs. normal hydrogen electrode

A) in 1,2-dichlorobenzene, B) in KBr, C) in methylene chloride/acetonitrile, D) vs. ferrocene, E) in carbon tetrachloride, F) in 1,1,2-trichloroethane at 90 °C, G) 1,1,2-trichloroethane at 70 °C

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

[*] peak potential, potential in parentheses indicate an irreversible redox reaction

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