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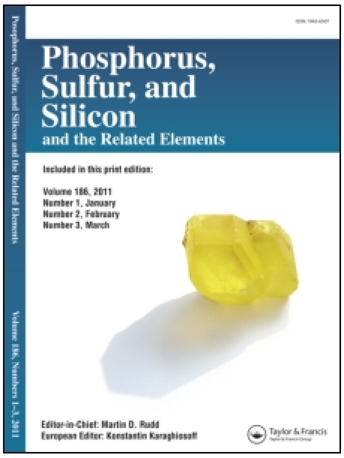

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RESULTS TOWARDS SYNTHESIZING THE POTENTIAL ELECTRICAL CONDUCTOR POLY(1,2-DITHIOLO-1,2-DITHIOLE-2,6-DIYLIDENE)

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Abstract Complex-catalyzed polymerization of bis-alkylthio-acetylenes 4 with nickel catalysts leads to the poly(bis-alkylthio-acetylenes) 2 ($\bar{P}_n$: 3-50). The influence of the catalysts, of the structure of the monomers and of the solvent on the polymerization is described. The polymers 2 are insulators and become semiconductors by doping with electron acceptors. Compounds 2 decompose thermically at temperatures higher than 250 °C by a splitting off of dialkyldisulfides, dialkylsulfides and alkanethioles. By laser-induced pyrolysis electrical conductors are formed.
The 4 are useful starting compounds for synthesizing dimeric 1,4-dithiafulvenes 8.
The 1,2-dithiole-thione 3a is available from 2,3-di-tert-butylthiofumarates or perchlorobutadiene with sulfuration reagents. The reactions of 3a with electrophiles and nucleophiles are studied. From 3a, the 3H,6H-2,5-bis-aryl-1,2-thiazolino[5,4-d]1,2-thiazoline-3,6-dithiones 28 are easily obtainable. Their isomerization to the 3H,6H-3,6-bisarylimino-1,2-dithiolo[4,3-c]1,2-dithioles 30 and vice versa, is described.

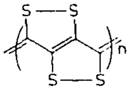
INTRODUCTION

In 1973 the high electrical conductivity of the TTF-TCNQ charge-transfer complexes was found.[1] This gave a powerful impulse to many work groups all over the world to deal with the synthesis and characterization of electrical conducting organic materials. The best results were obtained with reversible redox donors containing sulfur and selenium.

In these materials the chalcogene atoms play a very important role both as a component of the single donor molecule and also as coordinators between the different donor stacks in the solid state. A highlight of this development was the synthesis of the superconducting tetrachalcogenafulvalen complexes.[2]

In 1977 it was found that the resistance of the well known semiconducting polyacetylene decreases dramatically if it is oxidized under controlled conditions. This "doping" - e. g. with bromine, iodine or AsF_5 - leads to polymers with metal-like properties and conductivities of up to 10^3 Scm^{-1}.[3] Later many other polymers were doped, but the high conductivity of polyacetylene could not be reached. (Recently, a conductivity of $10^5 Scm^{-1}$ has been reported [3]).

The polymer of the type 1, the poly(dithiolo-dithiole-3,6-diylidene), is also a polyacetylene in which each carbon atom is substituted by an easily polarizable sulfur atom.



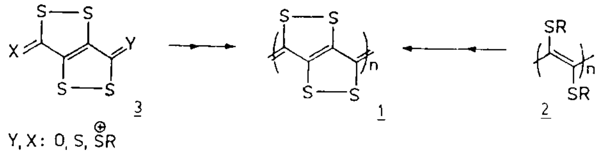
1

From this polymer we expect the following properties: planarity of the chain; an effective electronic interaction, both between sulfur atoms of neighboring dithiole rings and also between different polymer chains and a reversible redox behavior. We therefore suspect that it might have high electrical conductivity. These expectations are supported by the quantum chemical computations of HARTMANN.[4] He found, on the basis of a modified HMO-calculation, that in polymers of the type 1 the HOMO und LUMO overlap.

The polymer 1 represents one possible structure of poly-carbonmonosulfide that was prepared by DEWAR and JONES in 1910 by a spontaneous polymerization of monomeric CS.[5] (For more information see [6].) However, the real structure of poly-carbonmonosulfide is still unknown.

In 1986 ARMAND[7] published the synthesis of polymers with the structural elements of a dithiolo-dithiole-diylidene. He started with a polymer consisting of a chain of sp-hybridized carbon atoms, which was activated with lithium and then thiolated by sulfur. The resulting polymers, which can be synthesized with a variable sulfur content ranging from 0.15 to 1 per carbon atom, seem to be an attractive electrode material for batteries with a high capacity and energy density.

In order to synthesize the polymer 1 we selected two different courses of action.



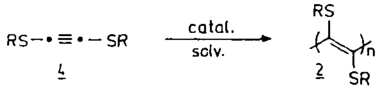
The first one was to synthesize polyacetylenes 2, then to remove the organic groups R and finally to connect the 1,3-standing sulfur atoms. The second way was to synthesize the "monomeric" dithiolo-dithioles 3 and to convert them into the target polymer. This paper deals with the results of both strategies and the chemistry of the compounds 2 and 3.

SYNTHESIS AND PROPERTIES OF POLY(BIS-ORGANYLTHIO-ACETYLENES) 2

Before we started our work polymers of the type 2 were unknown. There had only been reports about the polymerization of some mono-arylthioacetylenes.[8] These polymerizations were catalyzed with Lewis-acids or carried out thermically. Our attempts to use such conditions to polymerize bis-organylthio-acetylenes 4 were unsuccesful. Only oils were obtained.

Commonly used catalysts for acetylene polymerization are described by SHIRAKAWA[9] (aluminiumalkyls/titaniumalcoholates) and by LUTTINGER[10] (Ni(II)-complexes/$NaBH_4$). Such systems do polymerize the bis-organylthio-acetylenes 4, but side-processes such as the splitting off of the organyl and organylthio groups were observed.

We found simple Ni(II)-complexes of the type 5, -allyl-Ni(II)-complexes of the type 6, and some Ni(O)-complexes 7 to be suitable for the polymerization of 4.



2,4	
a	Me
b	Et
c	n-Prop
d	i-But
e	CH_2Ph
f	c-Hex

5	X	L
a	Cl	$P(Ph)_3$
b	Br	$P(Ph)_3$
c	I	$P(Ph)_3$
d	Br	$P(n\text{-}Bu)_3$
e	Br	$Ph_2P\text{-}CH_2\text{-}$

5: L_2NiX_2

6: $[<NiBr]_2$

7: $Ni[P(OPh)_3]_4$

solv. MeOH, THF, MeCN, $CHCl_3$

In particular, the systems 5 are of practical interest. They are very cheap, easy to produce and stable against air.

A series of bis-organylthio-acetylenes containing different-sized substituents R were polymerized. The results of the polymerization with bis-triphenylphosphine-Ni(II)-bromide 5b as catalyst are summarized in table 1 .

TABLE I Poly(bis-alkylthio-acetylenes)2[a]: number average molecular weight, degree of polymerization and yield dependence from solvent and the structure of the acetylenes 4; catalyst: 5b

2,4	solvent	$M_{\bar{n}}$	$P_{\bar{n}}$	yield (%)
a	THF	4380	37[b]	92[c]
a	MeCN	3120	26	40
b	THF	1260	9	23
b	MeCN	1130	8	75
c	THF	3410	20	32
c	MeCN	2350	14	24
d	THF	4450	22	9.5
d	MeCN	2420	12	15
e	THF	856	3	32
e	MeCN	840	3	60
f	MeCN	825	3[d]	15

---

[a] temperature: 20 °C; time: 72 h; molar ratio of catalyst to monomer: 1/70; [b] the values of $M_{\bar{n}}$ and $P_{\bar{n}}$ represent the fraction insoluble in THF; [c] whole yield (fractions soluble and insoluble in THF); [d] polymerization at boiling temperature of the solvent; reaction time: 2h

The products are brown to red-brown solids which are easily soluble in halogenated hydrocarbons. The elemental analysis corresponds to the expectations. Table 1 only considers the solid products. The oily products which are also formed are disregarded. The molecular weights were estimated by vapor-pressure osmometry.

TABLE II Polymerization of bis-methylthio-acetylene 4a to poly(bis-methylthio-acetylene) 2a[a) ; number average molecular weight, degree of polymerization and yield dependence from the solvent and the catalyst

solvent	cat.	2a yield (%)			$M_{\bar{n}}$		$P_{\bar{n}}$	
		b)	c)	d)	b)	c)	b)	c)
THF	5a	2.4	2.4	4.8	5000	3200	42	27
THF	5b	18.6	15.7	34.3	4500	2390	38	20
THF	5c	33.5	13.0	46.5	3190	1980	27	16
MeCN	5a	31.7	0	31.7	3600		31	
MeCN	5b	40.8	0	40.8	2950		25	
MeCN	5c	28.5	0	28.5	2540		21	
MeOH	5a	39.4	0	39.4				
MeOH	5b	39.7	0	39.7				
MeOH	5c	42.6	0	42.6				
MeCN	5d	27	0	27				
MeCN	5e	5	0	5				

a) temperature: 25 °C; time: 25 h; molar ratio of catalyst to monomer: 1/100; b) fraction precipitated during polymerization; c) fraction precipitated with methanol; d) sum from b) and c)

There is a clear tendency, whereby the bulkier the groups R, the lower are both the yields and the molecular weights. A possible reason may be the sterical hindrance of the polymerization process by the groups R. Secondary aliphatic groups completely suppress the polymerization at room temperature, but the yields are low even at elevated temperatures. The yields also depend on the solvent, but no regularities can be seen.

Using the example of bis-methylthio-acetylene 4a, the influence of the catalyst on the polymerization was investigated. The results are shown in table 2. In the range of the Ni(II)-halide-complexes the iodide 5c is the most active, followed by the bromide 5b. This graduation in catalytic activity was also found by others.[11] The average molecular weight of the polymers obtained increases from the iodide to the chloride complex. The differences between the complexes are leveled out in solvents where the complexes dissociate into their components, e. g. when in methanol. In this solvent the metal ions are equally coordinated, and consequently, there are no big differences in the catalytic properties. (In contrast to other solvents, it was found that in methanol products with a low solubility were obtained, and therefore an estimation of the molecular weight by vapor pressure osmometry was impossible). The stability of the Ni-phosphine-bond has a great influence on the catalytic activity. The stronger the metal-ligand-bond, the lower is the catalytic activity (catal. 5d, 5e). The Ni(II)- and Ni(0)-complexes 6 and 7 show catalytical activity comparable to the simple Ni(II)-complexes 5. From a practical point of view they are not so interesting, due to their poorer availability and reduced stability against air and moisture.

In our concept of the polymerization mechanism we follow results from the literature.[11, 12] We suppose a coordination of an acetylene molecule on the catalyst followed by the insertion of the acetylene in a ligand-metal-bond. Indeed, we have isolated a 1-to-1-complex of 5b and the acetylene 4a. The next steps in the polymerization are the coordination of a further molecule of acetylene and its insertion into a carbon-metal-bond, and so on. The molecular weights of the polymers, however, are low, and in comparison to many other polymerizations, a large amount of the catalyst is necessary for high yields of the polymer (acetylene to catalyst - 70:1). There must be some rupture processes that limit the polymerization. One possibility is the cleavage of the organyl-sulfur-bond. In fact, in the case of 4e we found that benzylbromide was formed when we tried to synthesize the complex between this acetylene and the complex 5b.

The solid state ^{13}C NMR spectra of the polymers 2 show the expected ratio of sp^2/sp^3-hybridized carbon atoms. This verifies the structure of these compounds as polyacetylenes. In comparison to the unsubstituted polyacetylene ($\lambda_{max} \approx$ 700 nm) the UV-VIS spectra of 2 show a maximum near 250 nm and broad absorptions of low intensity up to 800 nm. This indicates a highly twisted polymer backbone but no large conjugated π-electron-system. This non-planarity may be the reason for the insulating properties of polymers 2 (σ: 10^{-15} Scm^{-1}).

The low chemical stability of the halide-doped polymers may be a consequence of the basicity and nucleophilicity of the anions formed. If the polymers are doped with antimony(V)-chloride, more stable hexachloroantimonates are obtained. Also, with a large excess of dopand, no more than one anion per four monomer units could be introduced into the polymer. The products formed have a spin density of about 10^{21} spins/mol monomer unit. This indicates that closed shell cations predominate. The conductivity of these compounds is 10^{-9} Scm^{-1}.

We tried to achieve the reductive dealkylation of 2e with sodium in liquid ammonia. Unfortunately, both the sulfur-alkyl-bond and the sulfur-polymer backbone-bond were cleaved off.

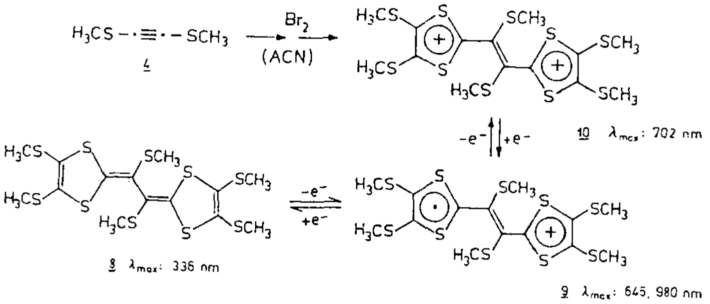
Other modifications of the polymers were the alkylation of the S-atoms under formation of sulfonium-ions and the oxidation with dinitrogen-tetroxide to polymeric sulfoxides. In both cases products with conductivities of about 10^{-10} Scm^{-1} were obtained.

The polymers 2 are photo-crosslinkable when they are irradiated with light up to 500 nm. The products formed are insoluble in common solvents. The crosslinking was detected by solid state ^{13}C NMR spectroscopy as a change from the sp^2-hybridized to sp^3-hybridized carbon atoms.

All the polymers 2 synthesized have a low thermal stability. DTA-investigations show a decomposition maximum at about 300 °C, independent of the polymer. This process is exothermic. Dialkyldisulfides, dialkylsulfides and mercaptanes are mainly formed as gaseous splitting products corresponding to the groups R. The residue is a black solid insoluble in all solvents. It is mainly composed of sp^2-hybridized carbon atoms and sulfur atoms.

If thin layers of the polymers are irradiated with laser light (argon ion laser, 488 nm), a pyrolysis also occurs. The resulting tracks have a metal-like shine and electrical conductivities of about 100 up to 500 Scm^{-1}. That is about 15 orders of magnitude higher than for the starting polymer. This pyro-conversion can be carried out with the high scanning speed of 5 to 8 meters per second and is of interest for producing circuit boards.

In our doping experiments of the polymers 2 with bromine we found a formation of deep blue colored salts when the monomers 4 were treated with bromine. These salts are reducable with zinc. The bromination products of 4a were investigated more precisely. Their reduction yields a mixture of about five light-yellow colored compounds. All these compounds are reversibly oxidizable and re-reducable. We isolated the main product by column chromatography. The structure 8 follows from X-ray analysis. The results of the ^{13}C NMR spectroscopy are in agreement with this structure. In the dimer 8 both the molecule halves are twisted against each other with an angle of 79,5 °. The oxidation leads to the di-cation 10 via the mono-cation-radical 9. The electrical conductivity of 10 is 10^{-9} Scm^{-1}.

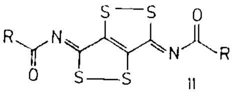


The polymers 2 are useable as active electrode materials in electrochemical elements. The experiments were carried out in cells with lithium as counter and reference electrode, propylenecarbonate/lithiumperchlorate as electrolyte and a polymer/carbon-black/PTFE-mixture as working electrode. The polymers 2 can be negatively and positively charged. After a formation process (about 3 cycles) the cells work reversibly and have a capacity of 62 mWh/g for the reductive and 160 mWh/g for the oxidative charge and discharge (values are related to the active electrode material).

ATTEMPTS TO SYNTHESIZE 1,2-TTF WITH AN EXTENDED -ELECTRON-SYSTEM

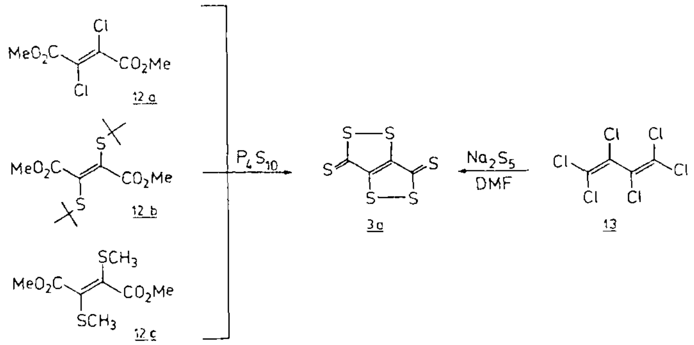
As mentioned above, our second strategy for synthesizing the polymer 1 was to start with "monomeric" dithioles 3. The formation of 1 from these monomers consists in the formation of 1,2-TTF-units. Syntheses of 1,2-TTF were described by BEHRINGER [13], PEDERSEN [14] and PAPAVASSILIOU [15]; for more details see also.[16] A common way to 1,2-TTF is the reductive dimerization of 3-chloro- or 3-alkylthio-substituted 1,2-dithiolium-salts.

The first dithiolo-dithioles described were the bisacylimino-derivatives 11.[17] But unfortunately, all attempts to remove the acylimino- or acyl-groups failed.



11

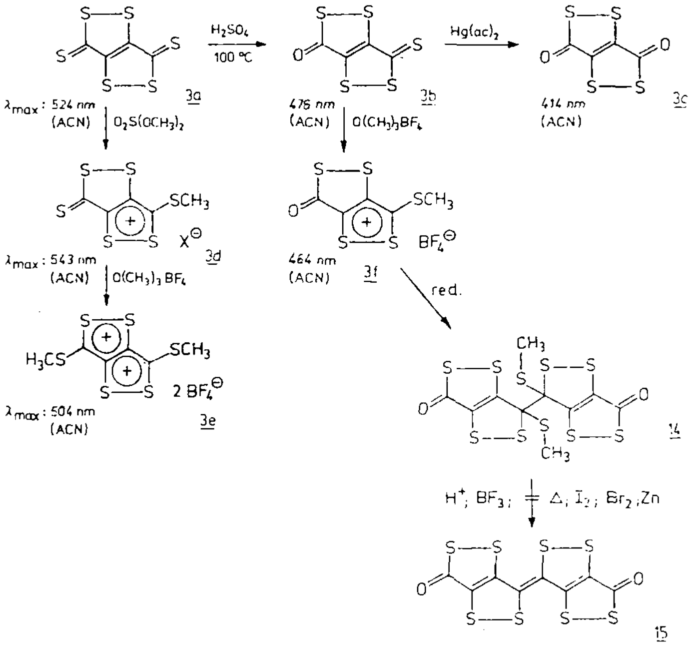
We found that a lot of linear C4-compounds activated by multiple bonds, halogensubstituents and/or carbonyl groups, e.g. 12a-c, yield the 3H,6H-1,2-dithiolo 4,3-c 1,2-dithiolo-3,6-dithione 3a when they are sulfurated. 12b generates the best results with a yield of about 15% [18]. However, this way cannot be recommended for obtaining 3a on a larger scale because the ester 12a must be prepared in a multi-step synthesis. In the thiolation of perchloro-butadiene 13 with sodium pentasulfide in DMF we found a convenient one-pot-synthesis of 3a, with yields of up to 30% of the theory. [19]



The dithione 3a is a violet, crystalline compound. The structure follows from the elemental analysis, mass spectrometry, IR and UV-VIS spectroscopy. The results of PPP-calculations agree well with the UV-VIS spectra measured. [20]

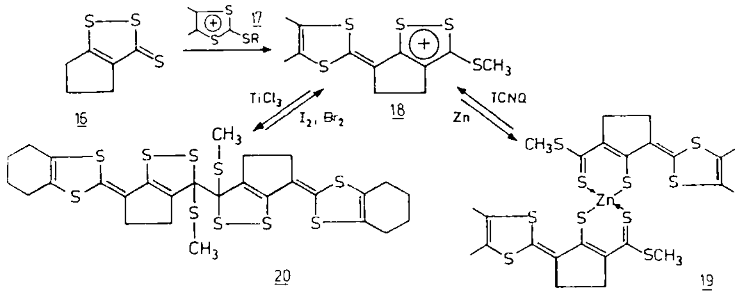
The reductive dimerization of the dithiolo-dithiole-system was the first step we were interested in. For this purpose the dithiolo-dithiolium-salts 3d-f were prepared by alkylation of the dithione 3a or the monothione 3b. The latter was obtained by heating the dithione in concentrated sulfuric acid.

If mercury(II)-acetate is used as the desulfurating agent, di-one 3c is the main product. All alkylation products, especially 3e , are very electrophilic and can be easily dealkylated. They are reducable with zinc dust or aqueous Ti(III)-chloride solution. In the case of 3f the dimer 14 could be isolated. The structure elucidation is based both on correct elemental analysis and on IR and UV-VIS spectroscopy. The spectra of 14 are similar to those of simple 1,2-dithiole-3-ones.



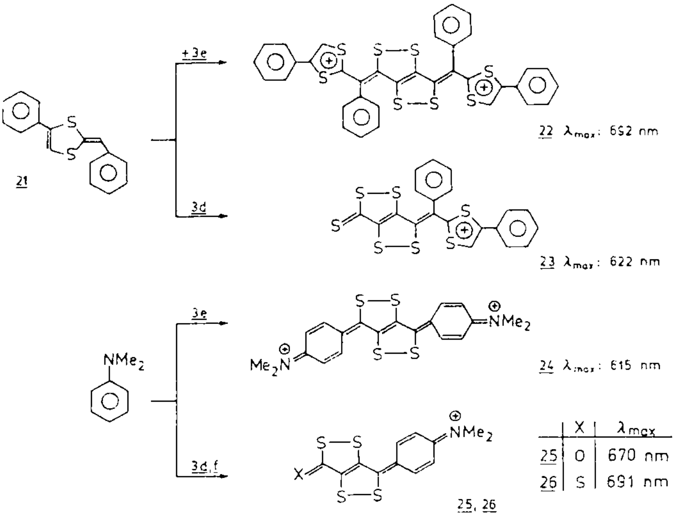
We tried to split off the methylthio-groups with several electrophiles; but either many products were formed (e.g. with sulfuric acid, bromine/zinc or zinc/acetylchloride) and no defined products could be isolated, or the dimer was halved (with bromine, silver-ion, antimony(V)-chloride or others). Obviously, it is more attractive to regenerate the "monomeric" dithiolium-ion 3f than to extract the methylthio groups under formation of the corresponding dication of 15. A possible explaination may be the very high electrophilicity of this dication and the sterical load of the single bond between the former monomers. Such oxidative de-dimerisation has also been observed in the case of simple 1,2-dithiole dimers.[21] Unsuccessful experiments for a reductive conversion of 14 to 15 (e.g., with triphenylphosphine or zinc) may be explained by the instability of the S-S-bond of the non-aromatic dithiole-ring in 14.

As model structures for studying the conversion of a 1,2-dithiolium salt with an extended π-electron system to the corresponding 1,2-TTF, we synthesized the cations 18. Starting from 1,2-dithiole 16 [22], condensation with the heterocyclium-salts 17 and following alkylation, many compounds of type 18 were synthesized. Reduction was tried with zinc dust and with an aqueous solution of titanium(III)-chloride. Using zinc as the reducing agent the zinc complexes 19, but not the dimers were formed. The complexes 19 are deep violet to blue colored compounds soluble in halogenated hydrocarbons. They can be re-oxidized to the dithiolium-ions 18. The reduction of a tetramethylene substituted 18 with titanium(III)-chloride in DMF gave a high yield of the dimer 20; but also in this case the attempts to convert 20 into a 1,2-TTF failed. Reduction of 20 with zinc dust, also in the presence of bromine as an extractor for the MeS-groups, yields the zinc complex 19. Attempts to achieve an oxidative extraction of the methylthio groups with bromine or other oxidants gave the monomeric dithiolium salt.



Therefore, the chemical behavior of the donor substituted dithiolium-salts 18 is similar to that of the acceptor substituted ones 3e-f. With both types of dithiolium-ions we were not able to get 1,2-TTF with an extended π-electron system.

For this reason, we looked for other possibilities to convert 3a or the 1,2-dithiolium-ions 3d-f into potential electrical conductors. We therefore condensed these compounds with some C- and N-nucleophiles[23].



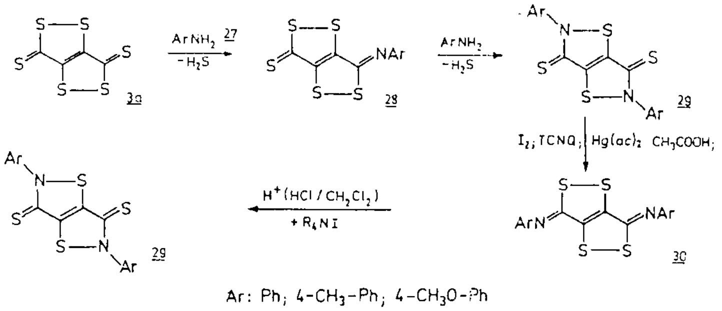
22 λ_{max}: 652 nm

23 λ_{max}: 622 nm

24 λ_{max}: 615 nm

	X	λ_{max}
25	O	670 nm
26	S	691 nm

With the 2-benzylidene-1,3-dithiole 21 the deeply colored polymethinedyes 22,23 and with dimethylaniline the compounds 24-26 were obtained. Another class we used for the condensation were the aromatic amines 27. When the reaction was carried out in acetic acid, the bis-imino-dithiolo-dithioles 30 were formed. In less polar solvents, e.g. toluene or tetrachloroethane, the isothiazolino[5,4-d]isothiazolines 29 were obtained. The monoimines 28 were isolated as intermediates.

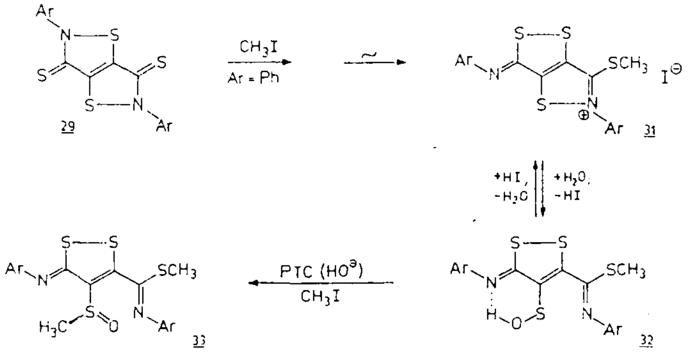


The isothiazolino-isothiazolines 29 represent both a new heterobicyclic system and the N-aryl-isothiazoline-3-thiones first described. The structure of the compounds 29,30 follows from the mass spectrometry (molecular peak). The fragmentation pattern of 29 and 30 differs, only 30 show a S_2-fragmentation and the backbone of the molecule - $Ar-N=C=C=C=C=N-Ar^{+}$- is a dominant fragment ion. The IR data ($\tilde{\nu}_{C=N}$ in the case of 30, $\tilde{\nu}_{CS}$ in the case of 29) are also in accordance with the structure proposed. The long wavelength absorption maximum of 30 lies at smaller values than that of 29. This agrees with PPP-calculations.

The dications 22,24 and the neutral molecules 30 are of interest as possible components in reversible redox systems. Investigations in this field are in progress.

From simple N-alkyl-1,2-dithiole-3-imines it is known that they can be transformed into the isomeric 2-alkyl-1,2-thiazoline-3-thiones, and vice versa.[23] There is also an equilibrium between the compounds 29 and 30. The bis-imines 30 are favoured in more polar solvents and in the presence of protons, whereas in less polar solvents the isothiazolino-isothiazolines 29 are favoured The rearrangement is reversible and can be catalyzed by protons in the presence of weak nucleophiles, e.g. iodide or thiourea. In the presence of larger amounts of protons or of oxidants such as iodine, bromine, TCNQ or Lewis acids, the conversion of the 29 into the bis-imines 30 is complete.

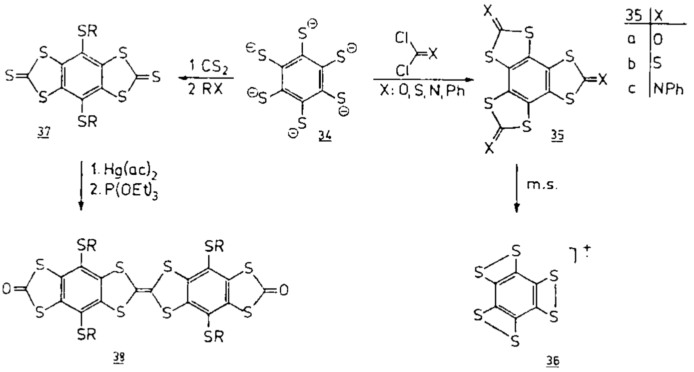
The isothiazolino-isothiazolines 29 generate some further interesting reactions, explained here with the example of the unsubstituted phenyl derivative. The alkylation with methyl iodide immediately produces the imino-dithiolo-isothiazolium salt 31.



The alkylation is connected with a rearrangement of one thiazoline ring to the 1,2-dithiole ring proven by the absence of the thiocarbonyl band in the IR spectra. The isothiazolium salt is unstable against water. The sulfenic acid 32 is formed by a ring opening reaction. The stability of this sulfenic acid - the pK-value is

8.4 - is caused by a hydrogen bonding between the hydrogen of the hydroxyl group and the nitrogen of the imine group. The hydroxyl group can easily be removed from the sulfenic acid by acetyl chloride or hydrogen iodide and under ring closure the imino-1,2-dithiolo-iso-thiazolium salt 31 is reformed. As expected, the alkylation of the sulfenic acid by methyl iodide in the presence of a base gave the sulfoxide 33. The ^{1}H NMR spectrum, the IR and the mass spectrum are in accordance with the sulfoxide structure.

Every attempt to obtain a structurally defined polycarbonmonosulfide failed. Therefore, we concentrated our activities on a reduced cyclic hexamer of carbonmonosulfide, the benzenehexathiolate 34. This compound is of great interest both as a complex ligand and as starting material for synthesizing new 1,3-TTF types. The hexaanion 34 has been known for some years and was obtained in HMPT solutions by reduction of hexakis-isopropylthio-benzene with sodium[24]. The isolation of a pure product 34 was not described. In the reduction of hexakis-benzylthio-benzene in liquid ammonia we found a convenient way to pure 34.



We were first interested in the highly symmetrical tri-4,5-(1,3-dithiolylenes).[35] These compounds are both building blocks for the synthesis of new TTF and precursors of organic ferromagnets.

The hexa-sodium benzene-hexathiolate 34 reacts with phosgene and its heteroanalogues to the tri-4,5-(1,3-dithiolylenes) 35a-c. These compounds were identified and characterized by UV, IR and mass spectrometry.[25] In the mass spectra of 35a and 35c the formation of 36 was observed. This is a very interesting molecule both from a theoretical and a synthetical point of view, and will be a subject of our future work. The reaction of 34 with carbondisulfide in DMF followed by alkylation leads to the tetrathia-s-indacene 37 [26], a precursor for the synthesis of polymeric TTF. For this purpose 37 was desulfurated with mercury(II)-acetate and the corresponding di-one was dimerized to 38, a reversible redox system. More detailed chemical and spectroscopical characterizations of the compounds are 34-38 in progress.

REFERENCES

1. L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, A. J. Heeger, Solid State Commun., 12, 1125 (1973).
2. K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen, J. C. Scott, J. Am. Chem. Soc., 103, 2440 (1981);
E. B. Yagubski, I. F. Suchegoglev, V. N. Laukhin, R. P. Shibaeva, E. E. Kostynchenko, A. G. Khomenko, Y. V. Sushko, A. V. Zvarykina, Pisma Zh. Eksp. Teor. Fiz., 40, 387 (1984);
J. M. Williams, T. J. Emge, H. H. Wang, M. A. Beno, P. T. Copps, L. N. Hall, K. D. Carlson, G. W. Crabtree, Inorg. Chem., 23, 2558 (1984);

H. H. Wang, M. A. Beno, U. Geiser, M. A. Firestone, K. S. Webb, L. Nunez, G. W. Crabtree, K. D. Carlson, J. M. Williams, L. J. Azevedo, J. F. Kwak, J. E. Schirber, Inorg. Chem., 24, 246 (1985).

3. H. Shirakawa, E. J. Louis, A. G. McDiarmid, C. K. Chiang, A. J. Heeger, J. Chem. Soc. (London), 1977 578;
Nachr. Chem. Tech. Lab., 35, 822 (1987).
4. H. Hartmann, I. Gutman, J. prakt. Chem., 325, 534 (1983).
5. J. Dewar, H. O. Jones, Proc. R. Soc. (London), 83, 408 (1910); Ibid. 85, 574 (1911).
6. E. K. Moltzen, K. J. Klabunde, A. Senning, Chem. Rev., 88, 391 (1988).
7. M. Armand, P. Degott, 3rd. Int. Meet. Lithium Batt., Ext. Abstr., Kyoto (Japan), 1986, 335.
8. G. G. Naumova, E. L. Brodskaya, A. Kh. Fillipova, M. G. Voronkov, Dokl. 4. Vses. Konf. Chim. Atsetilena, 3, 155 (1972).
C. Simionescu, Sv. Dimitrescu, V. Percel, Makromol. Chem., 95 (1971).
9. H. Shirakawa, S. Ikeda, Polym. J., 2, 231 (1971).
10. L. B. Luttinger, J. Org. Chem., 27, 1591 (1962).
11. W. E. Daniels, J. Org. Chem., 29, 2936 (1964).
A. Furlani, Gazz. Chim. Ital., 373 (1977).
12. C. Simionescu, Makrom. Chem., 163, 59 (1973).
13. H. Beringer, E. Meinetsberger, Tetrahedron Lett. 1975, 3473.
14. C. Th. Pedersen, J. Moller, Tetrahedron, 30, 553 (1974).
15. C. Papavassiliou, J. S. Zambounis, S. Y. Yiannopoulus, Chemica Scripta, 27, 261 (1987).
16. G. Schukat, A. M. Richter, E. Fanghänel, Sulfur Reports, 7, 155 (1987).
17. A. Reiter, P. Hansen, H. U. Kibbel, Z. Chem., 17, 221 (1977).
18. A. M. Richter, E. Fanghänel, Tetrahedron Lett., 24, 3577 (1983).
19. A. M. Richter, E. Fanghänel, Sulfur Letters, 3, 25 (1985).
20. E. Bauwe, A. M. Richter, G. Rasch, E. Fanghänel, T. Weller, Z. Chem.,24, 418 (1984).
21. C. Th. Pedersen, Angew. Chem., 86, 315 (1974).
22. R. Mayer, P. Wittig, J. Fabian, R. Heitmüller, Chem. Ber., 97, 654 (1964).
23. H. Böshagen, H. Feltkamp, W. Geiger, Chem. Ber., 100, 2435 (1967).
24. F. Maiolo, L. Testaferri, M. Tiecco, M. Tingoly, J. Org. Chem., 46, 3070 (1981).

25. A. M. Richter, N. Beye, E. Fanghänel, Z. Chem., 28, 284 (1988)
26. A. M. Richter, N. Beye, E. Fanghänel, Sulfur Letters, 6, 135 (1987).

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