S-Position Isomers of BEDT-TTF and EDT-TTF: Synthesis and Influence of Outer Sulfur Atoms on the Electrochemical Properties and Crystallographic Network of Related Organic Metals

Piétrick Hudhomme,* Soazig Le Moustarder, Christophe Durand, Nuria Gallego-Planas, Nicolas Mercier, Philippe Blanchard, Eric Levillain, Magali Allain, Alain Gorgues, and Amédée Riou[a]

Dedicated to Prof. Guy Duguay on his retirement.

Abstract: The synthesis and characterization of new modified tetrathiafulvalenes (TTF), the *S*-position isomers of BEDT-TTF and EDT-TTF, are described. The synthetic strategy presented in this work is based on an efficient and unprecedented two-step sequence for the conversion of a vicinal bis(hydroxymethyl) functionality into a disulfide ring. Different routes are discussed in terms of efficiency for the synthesis of the symmetric *S*-position isomer of BEDT-TTF and that of EDT-TTF. Their electrochemical properties are combined with data obtained from UV/Vis spectroscopy and orbital calculations, and the electronic influence of peripheral sulfur atoms on the neutral and oxidized species is discussed. The introduction of these outer sulfur atoms at the periphery of the TTF core gives rise to specific intermolecular S···S interactions in the corresponding organic materials. Crystallographic studies of radical cation salts synthesized upon electrocrystallization clearly showed that the network obtained is dictated by the outer sulfur atoms, which are responsible for a characteristic and unprecedented "windmill" array.

Keywords: BEDT-TTF isomers · crystal engineering · organic materials · sulfur heterocycles · tetrathiafulvalene

Introduction

Considerable interest is currently being devoted to tetrathiafulvalene (TTF) derivatives as highly promising π-electron donors and versatile systems presenting applications in many areas,[1] as well as to the elaboration of organic materials that display unusual electrical properties.[2] Consequently, rapid progress has been observed in this field thanks to various chemical modifications of the TTF framework.[3] Nevertheless, the excessive one-dimensional character of organic metals in the TTF series is responsible for limitations in their transport properties (Peierls distortions). The enhancement of the dimensionality is thus considered an important goal for stabilizing the metallic state at low temperatures and, in some cases, to give rise to superconductivity.

One of the most successful strategies for improving the electroconductive properties of related materials relies on the introduction of sulfur atoms at the periphery of the TTF skeleton. In particular, the well known sulfur-rich π-donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) has produced two-dimensional conductors and a large number of superconducting radical cation salts[4] endowed with the highest critical temperatures (Tc) in that series. In their solid state structures, strong sulfur–sulfur intermolecular interactions play an essential role in the well-defined two-dimensional character.[5]

We were interested in chemical modification of ET in order to modify the two-dimensional molecular network, thus developing a novel array of molecular conductors. From this viewpoint, we have concentrated our efforts on modifying the positions of the peripheral sulfur atoms, with the aim of establishing specific S···S contacts in the molecular arrangement of related materials. Such intermolecular interactions have also been proposed for π-donors that have peripheral sulfur atoms,[6] such as bis(ethylenethio)TTF (BET-TTF). Furthermore, the ability to form two-dimensional organic (super)conductors is not limited to the radical cation salts of symmetric TTF derivatives: dissymmetric donors are also

---

[a] Prof. P. Hudhomme, Dr. S. Le Moustarder, Dr. C. Durand,
Dr. N. Gallego-Planas, Dr. N. Mercier, Dr. P. Blanchard,
Dr. E. Levillain, M. Allain, Prof. A. Gorgues, Prof. A. Riou
Ingénierie Moléculaire et Matériaux Organiques
UMR 6501 Université d'Angers
2 Boulevard Lavoisier, 49045 Angers (France)
Fax: (+33) 2-41-73-54-05
E-mail: pietrick.hudhomme@univ-angers.fr

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2001 0947-6539/01/0723-5070 $ 17.50+.50/0

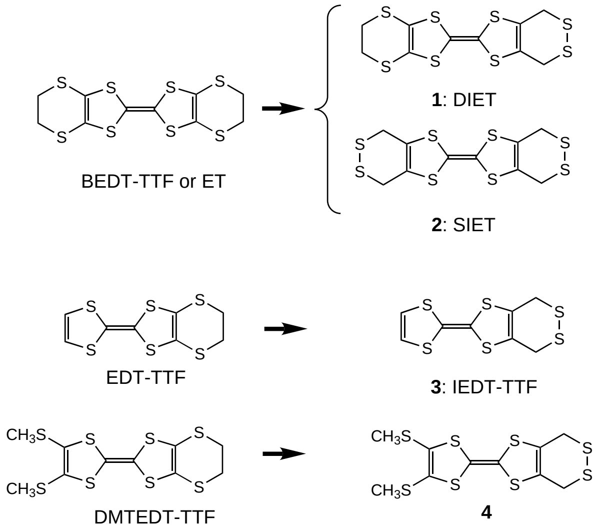
very attractive because of their tendency to crystallize into centrosymmetric dimers, thus favoring the so-called two-dimensional κ-phase network,[7] considered to be the passport to the generation of superconducting mixed valence salts in the TTF series.

Recently, we have been interested in the unprecedented dissymmetric[8] and symmetric[9] outer S-position isomers of BEDT-TTF. We now report the syntheses of DIET (*Dissymmetric Isomer of ET*, **1**) and SIET (*Symmetric Isomer of ET*, **2**) as well as their spectroscopic characterizations, electrochemical and orbital properties. We have also extended our synthetic approach to the development of the corresponding *S*-position isomers of EDT-TTF and DMTEDT-TTF: compounds **3** (named IEDT-TTF, for *Isomer of EDT-TTF)* and **4**, respectively (Scheme 1). This new disulfide functionality in the TTF series, common to targets **1**–**4**, appears to be of particular interest in understanding the nature of resulting intermolecular interactions in the crystal engineering of the molecular materials.

Results and Discussion

Definition of the strategy: The most appropriate retrosynthetic analysis to reach disulfide compounds consists of two successive functional modifications with the thioester group as an intermediate (Scheme 2a). By using this strategy, two different routes can be envisaged: i) the transformation of 2,3-bis(hydroxymethyl)TTFs **5a**–**c**, first developed by our group[10] for the synthesis of dissymmetric targets, or, specifically for the synthesis of SIET, tetrakis(hydroxymethyl)TTF **5d**,[11] and ii) the disconnection of the TTF central double bond, leading to 2-thioxo-4,5-bis(hydroxymethyl)-1,3-dithiole **6**[11b] as starting material (Scheme 2b).

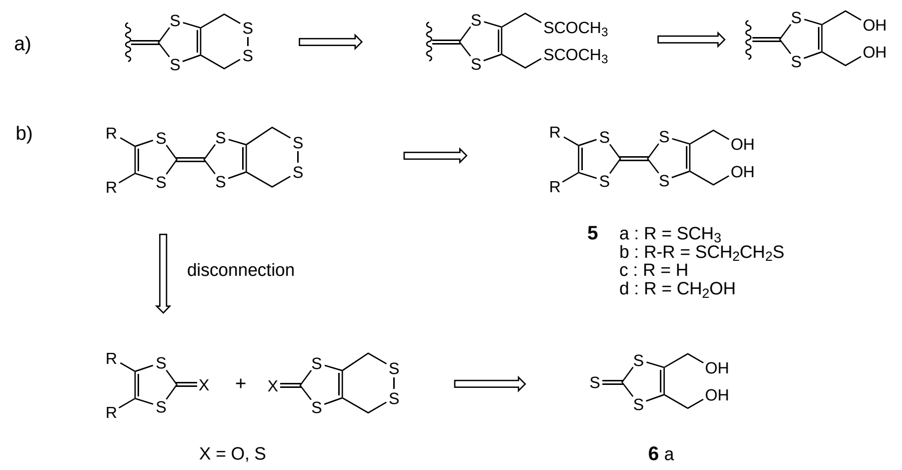
Abstract in French: *Les isomères de position des atomes de soufre périphériques du «fameux» BEDT-TTF ont été synthétisés et ont été nommés DIET et SIET, respectivement, pour isomères dissymétrique et symétrique de BEDT-TTF. La méthodologie de synthèse du pont disulfure terminal a été étendue, plus spécifiquement pour préparer l'isomère de EDT-TTF. Ainsi, la stratégie synthétique développée fait en particulier appel à une réaction originale d'activation des fonctions alcools des bis(hydroxyméthyl)TTF suivie d'un accès rapide au pont disulfure cyclique. Les propriétés électrochimiques sont également présentées, complétées par les calculs théoriques et propriétés optiques des donneurs à l'état neutre ou oxydé. L'influence de la position des atomes de soufre périphériques est clairement établie en comparant les structures cristallographiques des différents sels de cations radicaux de stœchiométrie équivalente issus de ces donneurs-π isomères de position. Ainsi, le rôle du pont disulfure dans l'organisation structurale s'avère déterminant dans la plupart des cas, et responsable d'un arrangement tout à fait original, dit «en moulin à vent», au sein duquel l'anion est localisé au centre de la cavité et les donneurs adoptant une organisation perpendiculaire les uns par rapport aux autres.*



Scheme 1. Target molecules as *S*-position isomers of BEDT-TTF, EDT-TTF, and DMTEDT-TTF.

Synthesis of DIET and the *S*-position isomer of DMTEDT-TTF (4): Historically, we have focused our attention on the synthesis of the dissymmetric targets **1** and **4** (Scheme 3).[8] Compounds **5a** and **5b** were prepared by following our previously reported synthetic strategy.[10] The trimethylphosphite-mediated cross-coupling of the two corresponding 2-(thi)oxo-1,3-dithiole moieties **7** and **8** afforded 2,3-bis(methyloxycarbonyl)TTFs **9a** and **9b**, respectively, in good yields. Further reduction of the ester functions was cleanly achieved by use of sodium borohydride/zinc chloride in THF under reflux to give 2,3-bis(hydroxymethyl)TTFs **5a** and **5b**.

We then investigated the generation of a good leaving group from the 2,3-bis(hydroxymethyl)TTF, in order to activate the nucleophilic substitution for conversion of the alcohol function into a thioester.[12] This problem was efficiently solved by using the Mitsunobu reaction.[13] The diethyl azodicarboxylate/triphenylphosphine (DEAD/PPh_3) complex reacted with 2,3-bis(hydroxymethyl)TTF (**5**), which allowed the activation of the alcohol function. Substitution could then occur in the presence of an acidic reagent, such as thioacetic acid. Following the experimental conditions previously reported for this type of reaction,[14] a mixture of dialcohol **5a** and thioacetic acid in THF was added dropwise to the DEAD/PPh_3 complex in THF at 0°C to give the bis(thioester)TTF **10a** in 58% yield. However, application of this Mitsunobu reaction to the 2,3-bis(hydroxymethyl)-6,7-(ethylenedithio)TTF (**5b**) was unsuccessful because of the well-known sensitivity of the ethylenedithio bridge to bases and nucleophiles.[15] To avoid this undesired reaction we considered another means of activating the hydroxymethyl group that involved *N*,*N*-dimethylformamide dineopentylacetal.[16] The analogous diethylacetal reagent was applied successfully to **5a** and **5b** and was finally preferred because of the easier subsequent purification of the bis(thioester)TTFs **10a** and **10b**, which were obtained in 58% and 60% yields, respectively. The one-pot reaction was carried out by using an

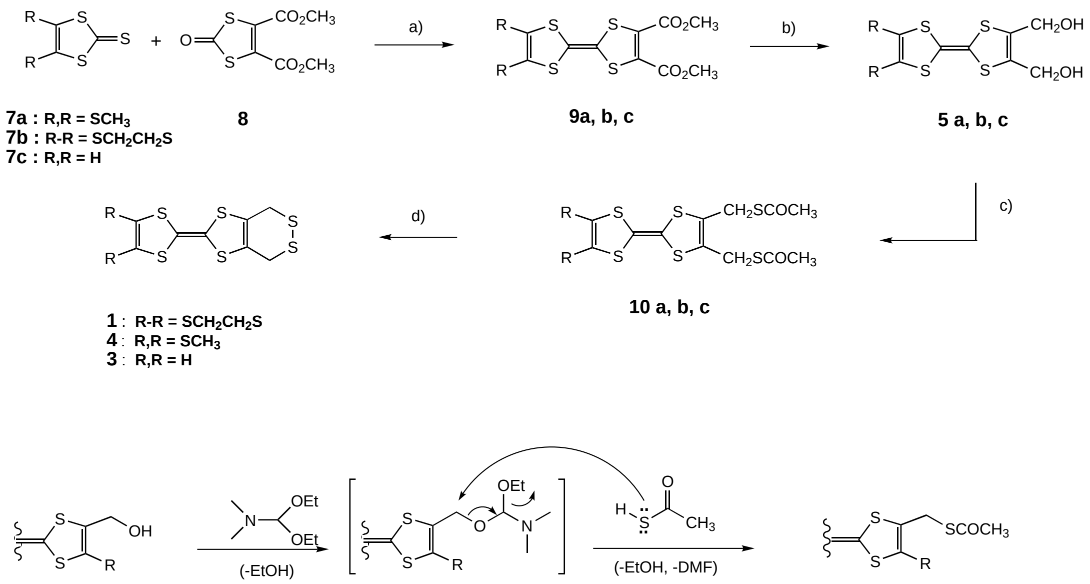


Scheme 2. Retrosynthetic scheme and starting materials.

excess of both activating reagent and thioacetic acid, and by following the proposed mechanism (Scheme 3).

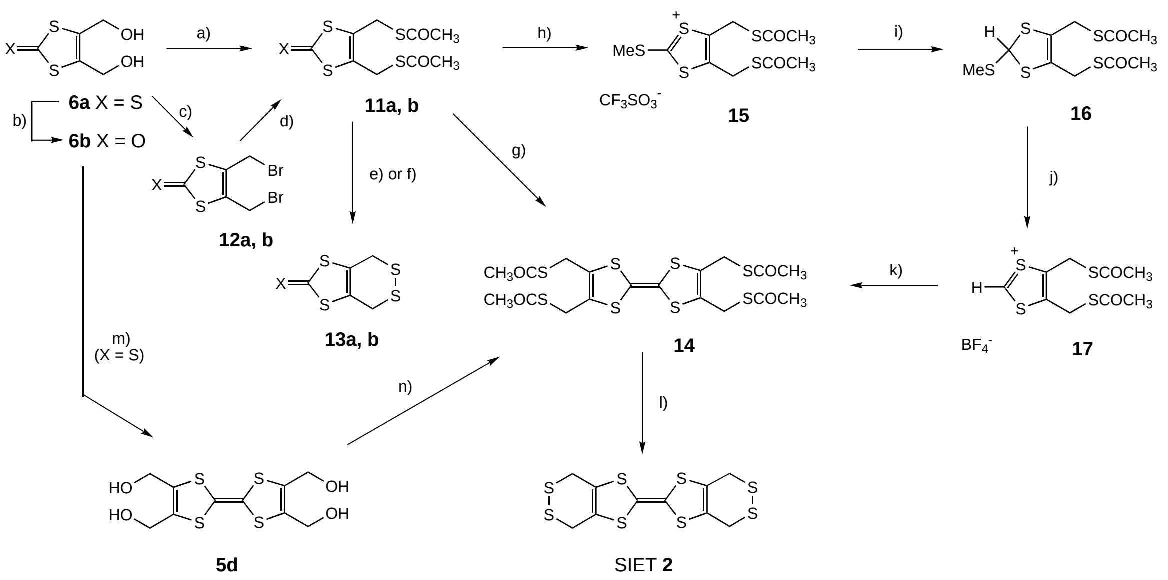
In order to reach the target disulfides, we initially prepared the dithiols[17] in 91 % and 96 % yields by reduction of **10a** and **10b** with DIBAl-H, respectively.[8] Further oxidation with DEAD,[18] iodine, or 2,2′-dithiobis(benzothiazole)[19] resulted in **1** and **4**. However, this strategy suffered from the modest yields (30–50 %) of this last step. Furthermore, we found that reduction of the bis(thioester)TTF, followed by oxidation to disulfide could be carried out with satisfactory yields in a one-pot reaction. Reduction was accomplished with sodium borohydride in the presence of lithium chloride in THF under reflux, and subsequent treatment with an aqueous solution of ammonium chloride efficiently afforded compounds **1** and **4**.[20] The *S*-position isomer of DMTEDT-TTF was easily purified by chromatography on silica gel and recrystallized from CH_2Cl_2/petroleum ether (93 % yield). Single crystals of this disulfide compound **4** were obtained and studied by X-ray diffraction.[8] DIET (**1**), on the other hand, showed poor solubility in CH_2Cl_2, estimated as ten times lower than that of BEDT-TTF itself. Consequently, compound **1** was first obtained as an analytically pure sample by filtration (88 %). In order to obtain crystals of the high purity necessary to accomplish further electrocrystallization experiments, we performed the purification using a short column of Florisil, with CS_2 as the eluent. Nevertheless, the best purification appeared to be by Soxhlet extraction with CS_2 for several days, affording pure orange microcrystals of DIET.

Synthesis of SIET: For the target SIET (**2**), we first considered the classical symmetric coupling reactions from corresponding 2-(thi)oxo-1,3-dithioles **13** (Scheme 4).[9] Initially, for the synthesis of **11**, our efforts were concentrated on the reactions previously applied in the TTF series for the preparation of **1** and **4**. After many experiments, the best results were obtained when the Mitsunobu reaction was used for **6a** and the activation with *N*,*N*-dimethylformamide diethyl acetal for **6b**. In both cases, compounds **11a** and **11b** were accompanied by undesired by-products and yields remained unsatisfactory (32 % and 52 %, respectively). The alternative route consisted of performing an easier nucleophilic substitution on analogous 4,5-bis(bromomethyl)-2-(thi)oxo-1,3-dithioles. Thus, diol **6a** was readily converted into **12a** by using phosphorus tribromide, in 94 % yield.[9, 21] Parallel to our work, the synthesis of **12a** was also achieved in 70 % yield by use of CBr_4/PPh_3 in a similar reaction.[22] Our strategy was then



Scheme 3. Synthetic strategy for DIET and the S-position isomers of DMTEDT-TTF and EDT-TTF. a) Δ, $P(OMe)_3$ (**9a**: 59%, **9b**: 60%, **9c**: 20%); b) $NaBH_4/ZnCl_2$, Δ, THF (**5a**: 83%, **5b**: 70%, **5c**: 61%); c) Method A: $DEAD/PPh_3$, CH_3COSH, THF (**10a**: 58%, **10c**: 51%) or Method B: $Me_2NCH(OEt)_2$, CH_3COSH, Δ, CH_2Cl_2 (**10a**: 59%, **10b**: 60%); d) $NaBH_4/LiCl$, Δ, THF then NH_4Cl/H_2O (**1**: 88%, **4**: 93%, **3**: 28%).

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2001



Scheme 4. Different synthetic strategies for the symmetric S-position isomer of BEDT-TTF (SIET). a) DEAD/PPh_3, CH_3COSH, THF (**11a**: 32%) or $Me_2NCH(OEt)_2$, CH_3COSH, CH_2Cl_2 (**11b**: 52%); b) $Hg(OAc)_2$, AcOH/$CHCl_3$ (44%), c) PBr_3, THF/CCl_4 (**12a**: 94%, **12b**: 62%); d) CH_3COSH, THF, Py (**11a**: 94%, **11b**: 98%) or $CH_3COS^-K^+$, THF (**11a**: 91%, **11b**: 89%); e) $NaBH_4$/LiCl, then NH_4Cl/H_2O (**13a**: 78%); f) MeO^-Na^+, MeOH then I_2/ether (**13b**: 85%); g) Δ, $P(OMe)_3$ (5%); h) CF_3SO_3Me, CH_2Cl_2 (98%); i) $NaBH_4$, *i*PrOH/CH_3CN (91%); j) HBF_4, Ac_2O (quantitative); k) Et_3N, CH_3CN (62%); l) MeO^-Na^+, MeOH/DMF (63%); m) Ref. [11b] MeI, THF (98%), $NaBH_4$, MeOH (90%), HBF_4, Ac_2O, then Et_3N, CH_3CN (77%), KOH, MeOH/THF/H_2O (92%); n) $Me_2NCH(OEt)_2$, CH_3COSH, Δ, THF(63%).

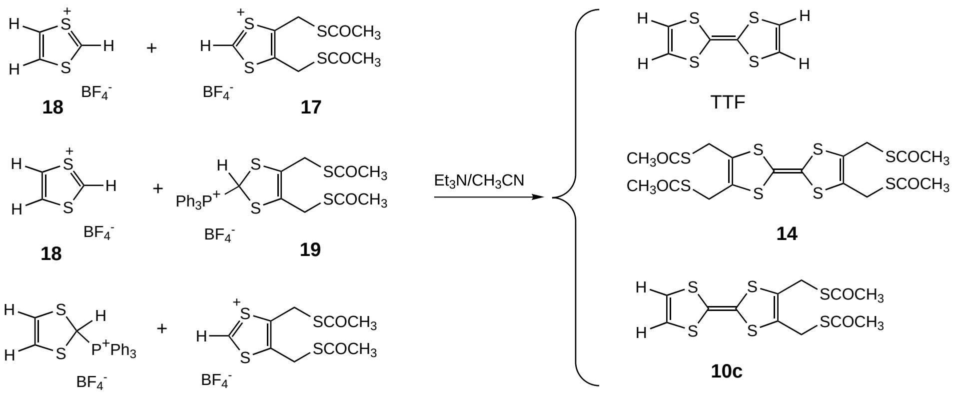
applied to the preparation of **12b** in 62% yield, but the easiest route to this compound remained the bromination of 4,5-dimethyl-2-oxo-1,3-dithiole by using *N*-bromosuccinimide (NBS).[23] After subsequent treatment of **12a** or **12b** with thioacetic acid (or potassium thioacetate), this route proved to be applicable on a large scale, compounds **11a** and **11b** being produced in excellent yields in both cases. Two different reactions were developed to obtain disulfide **13**. The previous method with sodium borohydride/lithium chloride followed by aqueous ammonium chloride solution treatment was applied successfully to give **13a** in 78% yield. We extended the development of the cleavage of the dithioester groups by considering their methanolysis. Thus, treatment of **11b** with sodium methoxide and subsequent treatment with iodine gave disulfide **13b** in 85% yield.

Unfortunately, attempts to achieve the trialkylphosphite-mediated coupling reactions from **11a** and/or **11b** failed, as did the dicobalt octacarbonyl method[24] from **11a**. In the case of precursor **11a**, trimethylphosphite coupling afforded the corresponding oxo derivative **11b**[25] in 70% yield and TTF **14** in only 5% yield. Concerning the coupling reaction from **13**, we noted the particular instability of the disulfide function under such drastic experimental conditions. Many hypotheses might explain this behavior: i) a possible retro-Diels–Alder reaction, resulting in the corresponding dienes upon heating.[26] Indeed, this is argued for by the presence in the mass spectra of peaks related to the dimethylidene[2*H*]-2-(thi)oxo-1,3-dithiole(s) from **13a** and **13b**, dimethylidene[2*H*]TTF from **1**, **3**, and **4**, and also tetramethylidene[4*H*]TTF from **2**, ii) the known reaction of trialkylphosphite with disulfides to afford corresponding sulfides,[27] iii) the scission of the sulfur–sulfur bond, which is favored under electrophilic, basic, or nucleophilic conditions.[27] This behavior was recently confirmed by Becher et al., who failed in the last step of their attempt to reach molecule **4** by another strategy.[28]

After these different failures in the coupling of 2-(thi)oxo-1,3-dithioles **11**, we considered an alternative route to reach the symmetric TTF **14**. Starting from **11a**, the 1,3-dithiolium cation salt **15** was first produced by methylation with methyl triflate in quantitative yield. Reduction to **16** with sodium borohydride in propan-2-ol/acetonitrile at 0°C (91% yield) was followed by dethiomethylation with fluoroboric acid in acetic anhydride to produce 1,3-dithiolium tetrafluoroborate **17** in quantitative yield. This was immediately treated with an excess of triethylamine in acetonitrile to give TTF **14** through carbenoid coupling in 62% yield. Transformation of **14** into the target *S*-position isomer of BEDT-TTF (**2**) was carried out with reagents described above for the similar conversions of **10a** and **10b** to **1** or **4**, but the yields were improved to 63% by treatment with a methoxide solution in methanol/*N*,*N*-dimethylformamide. The SIET compound was estimated to be three times less soluble in CH_2Cl_2 than BEDT-TTF itself, so it could be efficiently purified by silica-gel column chromatography with CS_2 as the eluent. Thus, this route provides clean and efficient access to the new symmetric *S*-position isomer **2** of BEDT-TTF.

Of course, we also studied the conversion of tetrakis(hydroxymethyl)TTF **5d** into TTF **14**. Because of its great insolubility, the tetraalcohol was suspended in THF and reacted progressively under reflux with an excess of *N*,*N*-dimethylformamide, diethyl acetal, and thioacetic acid to afford **14** in 63% yield after purification by column chromatography on silica gel.

Synthesis of the *S*-position isomer of EDT-TTF: Our previous success with the trimethylphosphite cross-coupling of an equimolecular mixture of corresponding 1,3-dithioles was encouraging for a generalization of this strategy. When applied to **7c** and **8**, the reaction effectively produced a mixture of the three possible TTFs: two symmetric ones and the expected dissymmetric product **9c**. Unfortunately, the dissymmetric TTF was obtained in this case only in a moderate 20% yield.[10c] Nevertheless, after reduction with $NaBH_4/ZnCl_2$ to afford the 2,3-bis(hydroxymethyl)TTF **5c** in 61% yield, we were able to apply the Mitsunobu procedure to prepare **10c** in 51% yield. This strategy was preferred to the acetal activation because of the easier purification of **10c** (Scheme 3). To avoid this unsatisfying reaction, we used the classical carbenoid coupling reaction[29] from the corresponding 1,3-dithiolium fluoroborate salts to produce symmetric or dissymmetric TTF derivatives (Scheme 5).[30] Such reactions were carried out with both 1,3-dithiolium salts **17** and **18**[29] in the presence of triethylamine and led to reproducible results when the experimental conditions described herein were followed. Thus, TTF (23%), dissymmetric compound **10c** (44%), and tetrakis(thioester)TTF **14** (18%) were successively separated by chromatography on silica gel. On the other hand, we also tried to take advantage of an approach, first developed by Cava[31] and recently applied to the synthesis of EDT-TTF,[32] involving a "pseudo-Wittig" condensation of 1,3-dithiole-2-triphenylphosphonium salts as ylide precursors, with 1,3-dithiolium salts as electrophiles. In the case of the reaction involving **18** and **19** (obtained in 98% yield by treatment of **17** with triphenylphosphine) in the presence of triethylamine, the dissymmetric TTF **10c** was produced in 28% yield, accompanied by TTF (49%) and the symmetric compound **14** (8%). As demonstrated previously,[33] the instability of a starting triphenylphosphonium salt in the presence of a base produced an equilibrium between **19** and **17**; this resulted in non-negligible amounts of symmetric TTF. This observation was confirmed by the subsequent reaction between **17** and **20**, which afforded TTF (10%), compound **14** (17%), and compound **10c** (63%); this result corresponding to the most efficient preparation of this precursor of the *S*-position isomer of EDT-TTF.



Scheme 5. Different routes to the *S*-position isomer of EDT-TTF.

The final step was performed by using sodium borohydride and lithium chloride in THF under reflux, followed by treatment with an aqueous solution of ammonium chloride. The resulting yield of disulfide **3** was dramatically lowered during the purification stage, however, no doubt because of its low stability during silica-gel or Florisil column chromatography (Scheme 3).

Electrochemical and spectroscopic properties; theoretical calculations: The cyclic voltammograms of ET, DIET, and SIET in CH_2Cl_2, and of EDT-TTF and IEDT-TTF in CH_2Cl_2/CH_3CN showed two reversible one-electron processes; this indicated successive generation of stable radical cations and dications at apparent redox potentials E^1_{app} and E^2_{app} (Table 1). The influence of the outer sulfur atoms on the redox potentials was particularly apparent on the second redox system and very weak on the first one. Indeed, the different electronic (inductive and mesomeric) effects of outer sulfur atoms should be discussed.

To go into more detail, theoretical calculations at the ab initio density functional level with the Gaussian 98 package[34] were performed in order to investigate the influence of the sulfur atoms on the molecular structure and the electronic properties of ET, DIET, and SIET. Becke's three-parameter gradient-corrected functional (B3LYP)[35] with a polarized 6–31G* basis was used for a full geometry optimization of the three isomers ET, DIET, and SIET in the neutral, radical cation, and dication states.

Neutral molecules: No significant differences were shown for the first oxidation peaks of neutral SIET, DIET, or BEDT-TTF (Figure 1). Indeed, molecular orbital analysis of the three isomers showed that the biggest HOMO coefficients were mainly located on the central TTF core (the $S_2C{=}CS_2$ fragment)[36] and that the energy values for the three HOMOs were very close (BEDT-TTF: −4.77 eV; DIET: −4.85 eV; SIET: −4.92 eV). Because of the very small contribution of the atomic orbital coefficients of the ethylenedithio group

Table 1. Cyclic voltammetry data for ET, DIET, and SIET[a] for EDT-TTF and IEDT-TTF.[b]

Compound	E^1_{app} [mV]	E^2_{app} [mV]	$E^1_{app} - E^2_{app}$ [mV]
ET	520	910	390
DIET	510	935	425
SIET	505	975	470
EDT-TTF	475	910	435
IEDT-TTF	485	945	460

[a] $c = 10^{-4}$ mol L^{-1} in 0.5 mol L^{-1} TBAHP, CH_2Cl_2; Pt electrode, ref. Ag/AgCl, scan rate 100 mV s^{-1}, 298 K. [b] $c = 1.4 \times 10^{-3}$ mol L^{-1} in 0.2 mol L^{-1} TBAHP, CH_2Cl_2/CH_3CN (9:1); Pt electrode, ref. Ag/AgCl, scan rate 100 mV s^{-1}, 298 K. CH_3CN was added to avoid adsorption phenomena at the electrode.

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2001

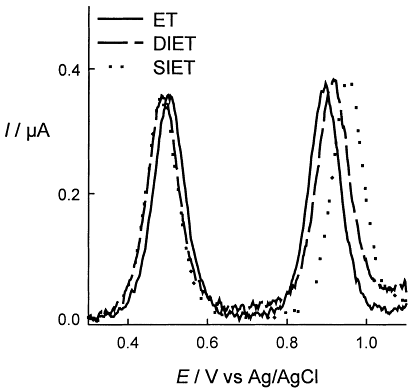


Figure 1. Comparison of BEDT-TTF, DIET, and SIET deconvoluted cyclic voltammograms.

sulfur atoms (S′) in the HOMOs of ET and DIET (0.1 coefficient), no significant mesomeric effect from the *S*-substituents should be expected (Figure 2).[37] No contribution at all was found for the outer sulfur atoms (S″) of the disulfide bridges of DIET and SIET.

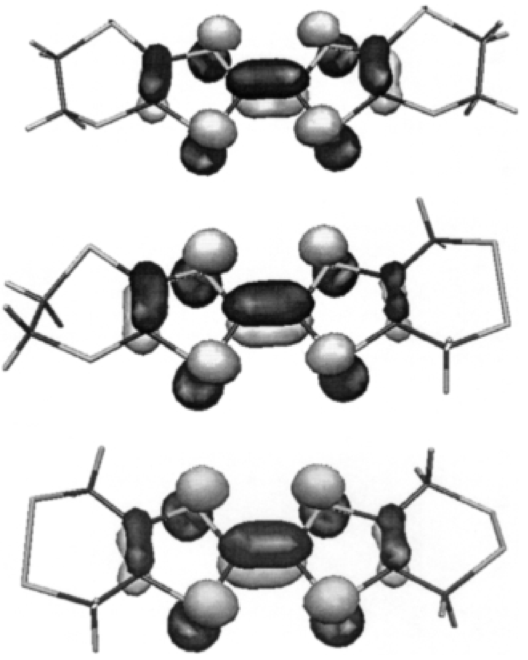


Figure 2. HOMO orbitals of ET (–4.77 eV; top), DIET (–4.85 eV; middle), and SIET (–4.92 eV; bottom) in the neutral state.

Consequently, only the electron-withdrawing inductive character of the sulfur atoms should be taken into account to explain the small differences observed for the three isomers, the sulfur atoms being further out in SIET than in BEDT-TTF. As previously shown by theoretical calculations on tetrathiafulvalene derivatives in the neutral state, the mesomeric effect of the sulfur atoms (S′) had no significant influence on their electron-donating ability.[38]

The electronic properties were then studied to complete the molecular-orbital analysis for these molecules. The UV/Vis data showed that the experimental absorption wavelengths for the three neutral molecules were fairly close in value (Table 2). Calculations were performed by using the new implementation of TD-DFT excitation energies,[39] and gave excitation energies that presented the same trend and showed good numerical agreement for the three neutral isomers (Table 2). As expected, the differences in the HOMO–LUMO gap estimated from electronic spectra for the neutral state did not significantly differ for ET, DIET, and SIET (the difference did not exceed 0.01 eV).

The optical properties of the radical cations and dications of ET, DIET, and SIET were also investigated by UV/Vis and near-IR spectroscopy, by addition of increasing amounts of $NOBF_4$ in CH_2Cl_2. Chemical oxidation resulted in the rapid disappearance of the neutral TTF derivative and in the development of new bands characteristic of the radical cation and then of the dication (Table 2). As expected, the electronic transitions of radical cation and dication were quasi-proportional to E^2_{app} for each compound (Figure 3).

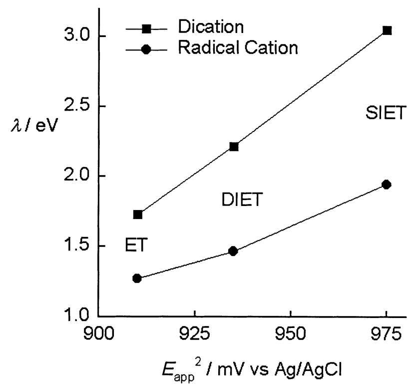


Figure 3. Variation of the energy of cation radicals and dications of ET, DIET, and SIET.

Radical cations: The most important effect relating to the introduction of disulfide bridge(s) became apparent with the second redox potentials, which shifted to more positive values (Figure 1), an effect that was also apparent for IEDT-TTF

Table 2. Experimental and calculated optical data for ET, DIET, SIET and their corresponding oxidized states.[a]

Compound	Neutral state		Radical cation state		Dication state	
	experimental [nm]	TD-DFT lowest excitation energy [nm]	experimental [nm]	TD-DFT lowest excitation energy [nm]	experimental [nm]	TD-DFT lowest excitation energy [nm]
ET	322[b]/346[b]/458	420 (98 → 100)	461[b]/577/975	1028 (98α → 100α)	718	840 (97 → 98)
DIET	311[b]/338[b]/466	463 (98 → 99)	424[b]/563/846	885 (98α → 100α)	559	691 (95 → 98)
SIET	314[b]/327[b]/474	480 (98 → 99)	446[b]/553/637	620 (98α → 100α)	406	462 (93 → 98)

[a] addition of $NOBF_4$ to 10^{-4} molL^{-1} in CH_2Cl_2 at room temperature. [b] maxima in the vibronic structure. The molecular orbitals involved in each transitions studied are indicated in brackets. Molecular orbitals 98 correspond to the HOMO for the neutral state, 98α and 98β to the HOMO and LUMO, respectively, for the radical cation state, and 97 to the HOMO for the dication state.

with respect to EDT-TTF (Table 1). Theoretical calculations with the unrestricted-B3LYP functional were then performed in order to study the differences in the optimized geometry and the molecular structure of the three radical cations. The optimized geometry found for the three isomers was perfectly planar, and a significant contribution of the π-sulfur atoms (S′) from the ethylenedithio group appeared in the HOMO orbital in both ET$^{\bullet+}$ and DIET$^{\bullet+}$, as well as the combination of π-atomic orbitals of the TTF core (Figure 4).

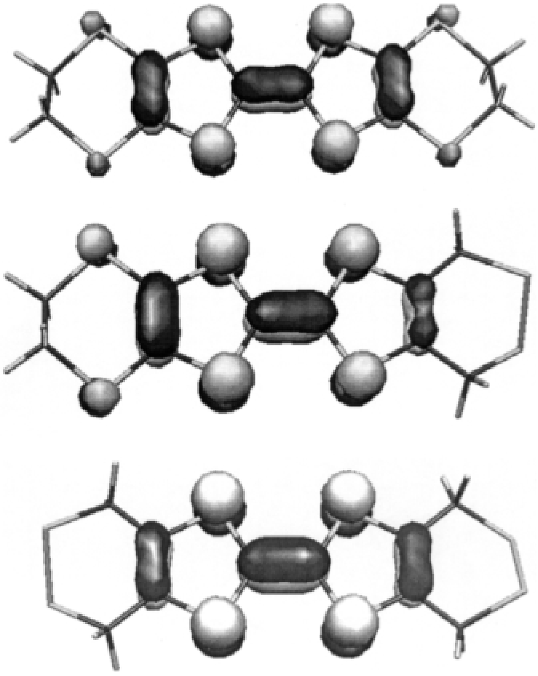


Figure 4. HOMO orbitals of radical cations ET$^{\bullet+}$ (−8.39 eV; top), DIET$^{\bullet+}$ (−8.67 eV; middle), and SIET$^{\bullet+}$ (−9.02 eV; bottom).

These changes could be explained by the existence of a mesomeric effect of the sulfur atoms, which stabilizes the radical cation. As expected, the outer sulfur atoms of SIET$^{\bullet+}$ did not show any contribution at all to the HOMO of the radical cation, since they could never participate in a mesomeric effect. The values obtained for the HOMO–LUMO gap followed the same trend as the UV/Vis data, showing a larger gap for SIET$^{\bullet+}$ (1.45 eV), than for DIET$^{\bullet+}$ (1.35 eV) and for ET$^{\bullet+}$ (1.26 eV). The lower excitation energies were also computed by the TD-DFT method; the values obtained matched the spectroscopic results and the previously calculated HOMO–LUMO gaps (Table 2). Moreover, these theoretical calculations confirmed that this broad and lowest energy band, observed at room temperature, must be assigned, as in the case of ET,[40] to the radical cation rather than to the corresponding π-dimer.[41]

Dications: Theoretical calculations carried out on the dication states of BEDT-TTF, DIET, and SIET provided evidence in this case of the existence of opposite electronic effects from the outer sulfur atoms. Full optimization of geometry carried out on ET^{2+} showed that the 1,3-dithiolium rings deviated by only 0.01° from planarity, in good agreement with the crystallographic structure of the dication salts BEDT-TTF $\cdot$ $(ClO_4)_2$ or BEDT-TTF $\cdot$ $(BF_4)_2$, in which no particular deviation between the two rings was observed.[42] In contrast, DIET^{2+} and SIET^{2+} presented distortions from planarity of 15.46° and 26.79°, respectively (Figure 5).

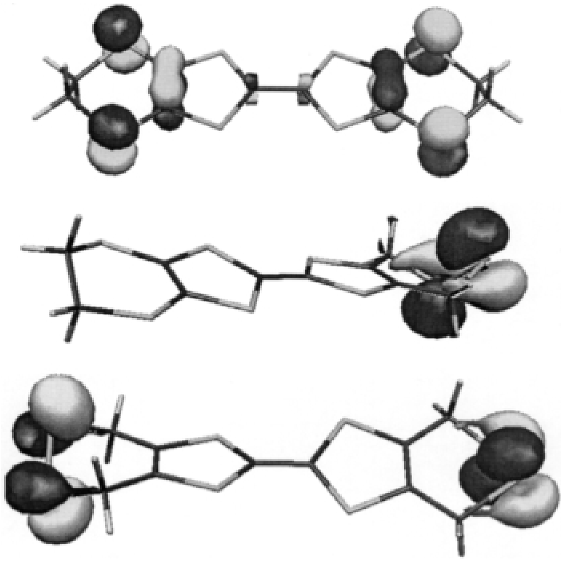


Figure 5. HOMO orbitals of dications ET^{2+} (−12.24 eV; top), DIET^{2+} (−12.08 eV; middle), and SIET^{2+} (−12.52 eV; bottom).

This structural peculiarity was unambiguously demonstrated with the DIET $\cdot$ $CuBr_4$ dication salt, which was obtained by chemical oxidation. In the crystallographic structure, this DIET^{2+} was characterized by an important distortion from planarity of 46° between the two dithiolium rings (Figure 6).

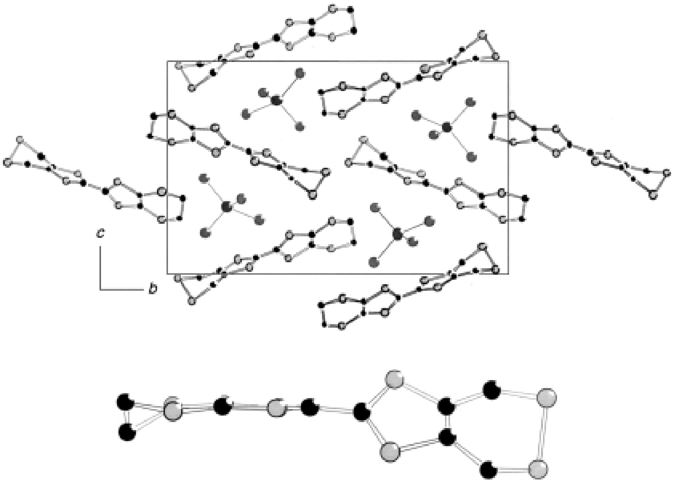


Figure 6. Crystal structure of DIET $\cdot$ $CuBr_4$: top: view of the structural layout; bottom: view of DIET^{2+}, showing the distortion of 46° between the dithiolium rings.

Molecular-orbital analysis performed on the optimized geometries gave a very different picture of the HOMO orbitals of the three dication isomers and completed the previous observations (Figure 5). The large contribution of the π-sulfur orbitals (S′) from the ethylenedithio group (0.4

coefficient), as well as the π-orbitals of the outer carbon of the TTF core (0.2 coefficient) and a slight contribution of the π-orbitals of the central carbon atoms in the TTF core (0.1 coefficient) show the strong π-character of this HOMO. This suggested a relevant argument for the existence of a mesomeric electron-donating effect from the outer sulfur atoms (S′) of the ethylenedithio groups in ET^{2+}. This mesomeric effect should induce planarity of ET^{2+} and stabilization of the dicationic state, thus explaining the lower measured second oxidation potential. In contrast, the main coefficients in this HOMO orbital belong only to the outer sulfur atoms in $DIET^{2+}$ and the four sulfur atoms in $SIET^{2+}$ (Figure 5). This important change in the electronic structure regarding the HOMO orbitals could be associated with an inductive electron-withdrawing effect of the outer sulfur atoms (S″) of the disulfide bridge(s) in $DIET^{2+}$ and $SIET^{2+}$ that would remove the electronic density away from the TTF core. It should be noted that the contribution of the sulfur atoms (S′) of the ethylenedithio group in $DIET^{2+}$ is only slight in orbital 96 (HOMO −1), but very important in orbital 95 (HOMO −2).

The lowest excitation energies obtained by the TD-DFT method are in agreement with the measured UV/Vis absorption bands (Table 2). For the ET^{2+} dication, the HOMO orbital still has a strong π-character and therefore the lowest transition corresponds to the HOMO–LUMO transition, implying molecular orbitals 97 to 98. In contrast, the electronic structures for $DIET^{2+}$ and $SIET^{2+}$ are altered completely, and the higher orbitals become σ in character. The molecular orbitals involved in π–π* transitions in $DIET^{2+}$ and $SIET^{2+}$ are lower lying in energy (molecular orbital 95 (HOMO −2) and molecular orbital 93 (HOMO −5), respectively). Consequently, the π–π* transitions for these two dications appear higher in energy. This might also suggest that the presence of outer sulfur atoms (S″) is responsible for the increasing σ-character of the HOMO orbitals.

The important torsion angle in the geometry of $DIET^{2+}$ and $SIET^{2+}$ may be related to increasing σ-character in the C–C central bond between the two 1,3-dithiolium moieties. This is supported by the optimized central bond lengths, computed as 1.41 Å for ET^{2+}, 1.43 Å for $DIET^{2+}$, and 1.44 Å for $SIET^{2+}$. Consequently, the increase in the torsion of the central bond and the loss of π-character are in good agreement with the hypsochromic shift found experimentally (Table 2).

Organic materials: Radical cation salts of different stoichiometries, including mixed valence salts, derived from *S*-position isomers of **1**, **2**, and **4** were prepared by electrocrystallization.[43, 44] To investigate the role of outer sulfur atoms in the intermolecular contacts between π-donors, we chose three significant examples to compare the crystallographic networks of two radical cation salts of identical stoichiometry that differed only in the positions of the outer sulfur atoms on the bridge: i) $DIET \cdot ClO_4 \cdot ½C_6H_5Cl$ and BEDT-TTF$\cdot ClO_4$, ii) **4**$\cdot ClO_4$ and DMTEDT-TTF$\cdot ClO_4$, and iii) $SIET_3 \cdot (ClO_4)_2$ and $(BEDT\text{-}TTF)_3 \cdot (ClO_4)_2$.

DIET·ClO₄·½C₆H₅Cl and BEDT-TTF·ClO₄: In the $DIET \cdot ClO_4 \cdot ½C_6H_5Cl$ salt, as is usual in BEDT-TTF salts, a layered structure with alternating planes containing anions and solvent molecules and planes of donors, is observed (Figure 7). Both molecules are packed in columns and form head-to-tail, centrosymmetric dimers with short distances (3.40 and 3.45 Å), showing significant molecular overlap. However, because of the strong tilting of dimers from the stacking axis (67°), weak S···S interdimer interactions are present (3.85 Å). The interesting feature in the structure of $DIET \cdot ClO_4 \cdot ½C_6H_5Cl$ salt results from the side-by-side S···S interactions along the *a* axis that are composed of: a) S···S contacts between sulfur atoms of the disulfide bridges of neighboring donors, and b) S···S contacts from sulfur atoms of the ethylenedithio group and sulfur atoms of the TTF core, these occur together. These interactions involving all the outer sulfur atoms seem to be partly responsible for the observed network in which a shift of dimers inside columns and a shift of neighboring columns are in evidence.

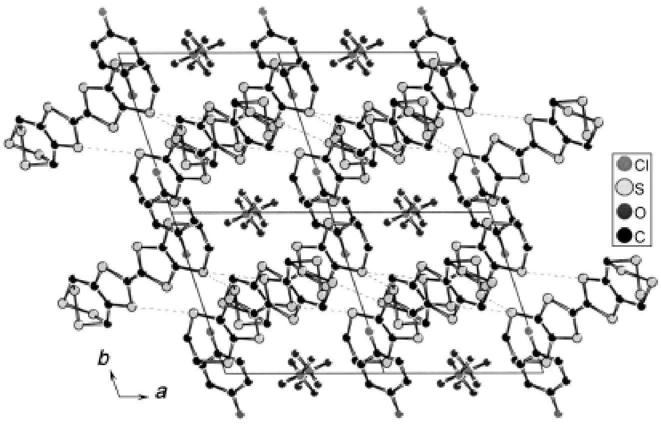


Figure 7. Projection onto the (*ab*) plane of the crystal structure of $DIET \cdot ClO_4 \cdot ½C_6H_5Cl$. S···S contacts smaller than the sum of the van der Waals radii are represented by dashed lines.

In the structure of the ε-BEDT-TTF$\cdot ClO_4$ salt,[45] in which the formal charge on BEDT-TTF is also +1, intermolecular S···S contacts between all the outer-ring sulfur atoms (d = 3.479(4) Å) are encountered with a staggered side-by-side mode of interaction. However, these strong S···S contacts do not imply a shift of donors in the regular stacks, in which a face-to-face mode occurs, but with no significant intermolecular interaction. As a consequence, the shift of neighboring columns appears more important in the structure of ε-BEDT-TTF$\cdot ClO_4$ than that observed in the structure of $DIET \cdot ClO_4 \cdot ½C_6H_5Cl$.

In conclusion, this particular organization of DIET donors in the radical cation salt is due to the concomitant presence of both disulfide and ethylenedithio bridges, columns of donors being shifted in order to engage outer sulfur atoms of the disulfide bridge and sulfur atoms of the ethylenedithio group in van der Waals interactions.

***4*·ClO₄** and DMTEDT-TTF*·ClO₄*: In the salt **4**$\cdot ClO_4$, donor molecules are stacked along the *a* axis in a head-to-tail manner, their mean molecular plane being perpendicular to the *a* axis. Inside columns, donors are dimerized, with intra- and interdimer distances of 3.44 and 3.59 Å, respectively. The principal characteristic of the crystallographic network is the tetragonal arrangement of donors in a "windmill" pattern and the localization of anions in the cavity created inside the "windmill" (Figure 8).[8, 44a] To our knowledge, such an array has been only described in TTF(Z) (with $Z = Cl$, Br, or I and $\rho = 0.77$, 0.76, or 0.77, respectively)[46] and in the $(TMTPDS)_2AsF_6$ salt.[47] In the $\mathbf{4} \cdot ClO_4$ salt, this typical perpendicular organization in the *bc* plane results from significant S···S contacts (3.51 and 3.55 Å) between sulfur atoms of the donor disulfide bridge and sulfur atoms of the TTF core of neighboring donors.

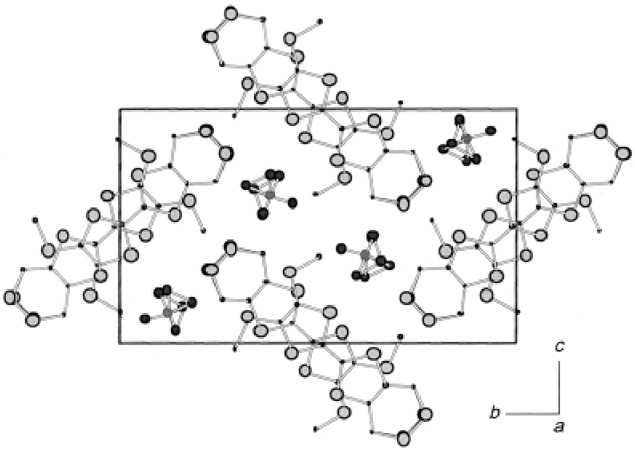


Figure 8. The original "windmill" network of donors **4** and disordered ClO_4 anions in the projection onto the (*bc*) plane of the crystal structure of the salt $\mathbf{4} \cdot ClO_4$.

The crystallographic network of the not previously described DMTEDT-TTF·ClO_4 is characterized by dimerized columns separated by perchlorate anions (Figure 9). Columns are composed of face-to-face centrosymmetric dimers of DMTEDT-TTF, in which a strong S···S π-orbital overlap is observed. In contrast, the intradimer molecular overlap is missing, a result of the tilting of donors with regard to the stacking axis. Consequently, the structure of DMTEDT-TTF·ClO_4 may be compared to an ionic-type structure, in which $(DMTEDT\text{-}TTF)_2^{2+}$ dimer units are surrounded by perchlorate anions.

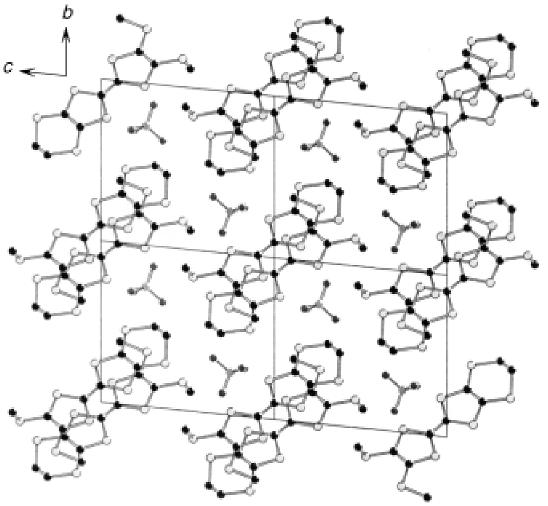


Figure 9. Projection onto the (*bc*) plane of the crystal structure of DMTEDT-TTF · ClO_4.

The structure of DMTEDT-TTF·ClO_4, surprisingly unlike the layered structures often encountered in EDT-TTF-derived salts, also appears very different from the structure of $\mathbf{4} \cdot ClO_4$. In the latter, the fundamental role of the outer sulfur atoms of the donor is underlined by the establishment of the "windmill" array.

$SIET_3 \cdot (ClO_4)_2$ and $(BEDT\text{-}TTF)_3 \cdot (ClO_4)_2$: The association of the symmetric *S*-position isomer SIET with the ClO_4^- anion affords a radical cation salt with the same [3:2] stoichiometry as that formed from BEDT-TTF $[(BEDT\text{-}TTF)_3 \cdot (ClO_4)_2]$.[48] In the semiconductor $SIET_3 \cdot (ClO_4)_2$ ($\sigma_{RT} = 10^{-2}\,S\,cm^{-1}$), donors are organized in centrosymmetric trimers, which are stacked along the *a* axis. Interplanar short distances (3.33 Å) and some short S···S contacts inside a trimer provided evidence of strong interactions between donors. Nevertheless, the weak intertrimer molecular overlap (shorter distances of 3.745 Å) is certainly responsible for the observed semiconductor behavior of this mixed-valence salt. The network is organized in trimerized stacks and the organic columns are oriented in the lattice so as to engage outer sulfur atoms of both disulfide bridges in van der Waals contacts. Consequently, this salt derived from the donor SIET also displays the characteristic "windmill" array (Figure 10); this association mode of the network being unambiguously associated with the presence of the terminal disulfide bridges, the arrangement differing from the general alternation of donor layers that characterizes BEDT-TTF salts.

The $(BEDT\text{-}TTF)_3 \cdot (ClO_4)_2$ salt[48] displays a layered structure, as encountered in most BEDT-TTF salts with alternating

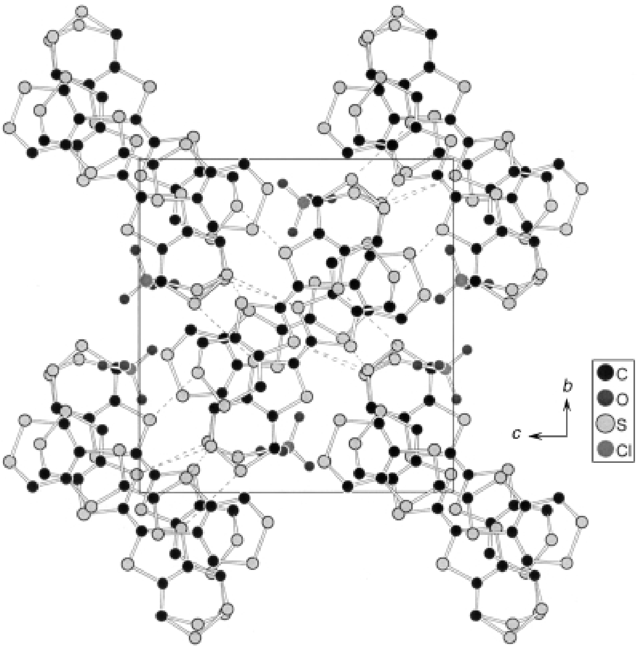


Figure 10. Projection onto the (*bc*) plane of the crystal structure of $(SIET)_3 \cdot (ClO_4)_2$, characterized by the "windmill" array. S···S contacts smaller than the sum of van der Waals radii are represented by dashed lines.

organic sheets and anion layers. In the donor array, strong transverse side-by-side S···S interactions occur, while no intermolecular contact along the stacking axis is evidenced. Consequently, the metallic state of $(BEDT\text{-}TTF)_3\cdot(ClO_4)_2$ became unstable, and a metal-insulator came into being at 170 K.

Conclusion

Efficient and original synthetic methodologies for obtaining different *S*-position isomers of BEDT-TTF and EDT-TTF, introducing outer disulfide ring(s) on the TTF core, are described. Their π-donor ability makes them good candidates for the preparation of organic metals. Firstly, the electronic effect of the peripheral sulfur atoms' positions were clearly demonstrated by a correlation between electrochemical and spectroscopic studies, completed with theoretical calculations on neutral and oxidized states. Secondly, the role of the terminal disulfide bridge(s) in the association mode of the network was established. Despite the poor contribution of outer sulfur atoms of the disulfide bridge in the HOMO, most of the electrogenerated radical cation salts display interesting structural features, with evidence of S···S contacts that are responsible for the crystallographic organization of donors, especially in the case of the characteristic "windmill" organization. While most of the resulting materials exhibit semiconductor behavior, electro-oxidations in the presence of various anions are currently under investigation. The role of peripheral sulfur atoms in the solid state network having been demonstrated, other radical cation salts with two-dimensional or even three-dimensional structural organizations are to be expected in the future from this new promising series of π-donors.

Experimental Section

General procedures: The following chemicals were obtained commercially and were used without any purification. Dry solvents were obtained by distillation over suitable desiccants (THF and toluene from Na/benzophenone, CH_2Cl_2 from P_2O_5, CH_3CN from CaH_2). Thin-layer chromatography (TLC) was performed on aluminium sheets coated with 60 F_{254} silica gel (Merck 5554). Column chromatography was carried out on 60 silica gel (Merck 9385, 230–400 mesh) or Florisil (Acros, 100–200 mesh). Melting points were determined by using a microscope with a Kofler hot stage and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Brucker AC200 (200 MHz) spectrometer. Chemical shifts are reported as δ values in ppm downfield from internal TMS. In ^{13}C NMR spectra, only characteristic peaks are reported. Mass spectra were recorded on a HP 5889 A spectrometer at 70 eV. IR spectra were recorded with a Brucker IFS 45 WHR spectrometer. Elemental microanalyses were performed by the Central Service of Microanalysis of the CNRS (Vernaison, France). Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum millielectrode of 7.85×10^{-3} cm^2 area and a platinum wire counter electrode. An Ag/AgCl electrode checked against the ferrocene/ferricinium couple before and after each experiment was used as reference. The electrolytic media involved CH_2Cl_2 (HPLC grade) and 5×10^{-1} mol L^{-1} tetrabutylammonium hexafluorophosphate (TBAHP—Fluka puriss quality). All experiments were carried out in solutions previously degassed by argon bubbling at 298 ± 0.5 K. Electrochemical experiments were carried out with an EGG PAR 273 A potentiostat with positive feedback compensation. On the basis of repetitive measurements, absolute errors on potentials were found to be around ±5 mV. UV/Vis and near-IR experiments were performed with a Perkin–Elmer Lambda 19 NIR spectrometer.

2,3-Bis(acetylthiomethyl)-6,7-bis(methylsulfanyl)tetrathiafulvalene (10a): Diethyl azodicarboxylate (0.64 mL, 4 mmol) was added dropwise at 0 °C under argon to a solution of triphenylphosphine (1.05 g, 4 mmol) in anhydrous THF (5 mL). After this mixture had been stirred at 0 °C for 15 min, a solution of 2,3-bis(hydroxymethyl)TTF (**5a**, 0.356 g, 1 mmol) and thioacetic acid (0.29 mL, 4 mmol) in THF (15 mL) was added dropwise. The dark solution was stirred at 0 °C for 1 h and then at room temperature for 1 h. The reaction mixture was dissolved in CH_2Cl_2 (150 mL) and washed with water (3 × 60 mL). The organic phase was dried ($MgSO_4$) and concentrated, and the residue was purified by flash column chromatography (silica gel, petroleum ether/CH_2Cl_2 1:1). Recrystallization (CH_2Cl_2/petroleum ether) gave orange crystals of the bis(thiolester)TTF **10a**. Yield: 0.274 g, 58 %; m.p. 104–106 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=3.95$ (s, 4H; CH_2S), 2.40 (s, 6H; SCH_3), 2.38 (s, 6H; $COCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=194.20$ (2C; C=O), 30.32 (2C; COCH_3), 26.54 (2C; C-CH_2-S), 19.16 (2C; SCH_3); IR (KBr): $\tilde{\nu}=1683$ and 1698 cm^{-1} (C=O); MS (70 eV, EI): *m*/*z* (%): 472 (62) $[M]^{\cdot+}$, 322 (95), 307 (15), 249 (23), 97 (30), 83 (35), 69 (44), 57 (51), 55 (56), 43 (100); elemental analysis calcd (%) for $C_{14}H_{16}S_8O_2$ (472.76): C 35.57, H 3.41, S 54.25; found C 35.69, H 3.35, S 54.07.

2,3-Bis(acetylthiomethyl)-6,7-(ethylenedisulfanyl)tetrathiafulvalene (10b): *N*,*N*-Dimethylformamide diethyl acetal (1.4 mL, 8 mmol) and thioacetic acid (0.58 mL, 8 mmol) were added to a solution of 2,3-bis(hydroxymethyl)TTF (**5b**, 0.354 g, 1 mmol) in anhydrous CH_2Cl_2 (70 mL). The solution was stirred at reflux for 48 h under nitrogen. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water (2 × 100 mL), dried ($MgSO_4$), and concentrated. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc 4:1) to afford yellow-ochre crystals after recrystallization (petroleum ether/EtOAc). Yield: 0.280 g, 60 %; m.p. 124–126 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=3.94$ (s, 4H; -CH_2S-CO), 3.27 (s, 4H; SCH_2CH_2S), 2.37 (s, 6H; $COCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=194.24$ (2C; C=O), 30.32 (2C; COCH_3), 30.26 (SCH_2CH_2S), 26.47 (2C; C-CH_2-S); MS (70 eV, EI): *m*/*z* (%): 470 (51) $[M]^{\cdot+}$, 442 (17), 322 (17), 320 (44), 292 (16), 88 (21), 43 (100); elemental analysis calcd (%) for $C_{14}H_{14}S_8O_2$ (470.78): C 35.71, H 3.00, S 54.49; found C 35.81, H 2.93, S 54.29.

2,3-(2,3-Dithiabutane-1,4-diyl)-6,7-(ethylenedisulfanyl)tetrathiafulvalene (1): A solution of the bis(thioester)TTF **10b** (71 mg, 0.15 mmol) in dry THF (10 mL) was added dropwise at 0 °C under nitrogen to a suspension of sodium borohydride (38 mg, 1 mmol) and anhydrous lithium chloride (5 mg, 0.1 mmol) in dry THF (10 mL). The reaction mixture was allowed to reach room temperature and was then stirred at reflux for 1 h. The solution was cooled to 0 °C and quenched with ice-water (5 mL) and a saturated solution of ammonium chloride (10 mL). The reaction mixture was stirred overnight at room temperature to precipitate compound **1**. The orange crystals were filtered, washed several times with dry methanol, and dried under vacuum to afford analytically pure DIET (**1**, 51 mg, 88 %). Further purification could be achieved by Soxhlet extraction with CS_2 for several days. M.p. 236–238 °C; ^1H NMR (200 MHz, CS_2 + $CDCl_3$): $\delta=3.45$ (s, 4H; CH_2SSCH_2), 3.27 (s, 4H; SCH_2CH_2S); MS (70 eV, EI): *m*/*z* (%): 384 (15) $[M]^{\cdot+}$, 322 (32), 320 (100), 294 (17), 292 (64), 216 (15), 172 (47), 88 (45), 76 (57), 64 (22), 52 (33); elemental analysis calcd (%) for $C_{10}H_8S_8$ (384.692): C 31.22, H 2.10, S 66.68; found C 30.98, H 2.09, S 66.09.

2,3-(2,3-Dithiabutane-1,4-diyl)-6,7-bis(methylsulfanyl)tetrathiafulvalene (4): This compound was prepared by the same experimental procedure that afforded **1**, with $NaBH_4$/LiCl. At the end of the reaction, after hydrolysis and extraction with EtOAc, the residue was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2 1:1) to afford orange-red crystals. Yield: 93 %; m.p. 173–174 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=3.48$ (s, 4H; CH_2SSCH_2), 2.42 (s, 6H; SCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=30.42$ (2C; CH_2SSCH_2), 19.20 (2C; SCH_3); MS (70 eV, EI): *m*/*z* (%): 386 (16) $[M]^{\cdot+}$, 324 (29), 322 (100), 307 (29), 274 (16), 172 (21), 118 (13), 103 (12), 91 (14), 88 (14); elemental analysis calcd (%) for $C_{10}H_{10}S_8$ (386.708): C 31.06, H 2.61, S 66.34; found C 31.16, H 2.52, S 65.85.

4,5-Bis(bromomethyl)-2-thioxo-1,3-dithiole (12a): PBr_3 (0.31 mL, 3.25 mmol) was added dropwise to a solution of the diol **6a** (450 mg, 2.32 mmol) dissolved in anhydrous THF (5 mL) and anhydrous CCl_4 (10 mL). The resulting light solution and orange precipitate were stirred under argon at room temperature for 5 h. The reaction mixture was treated with aqueous HCl (3 N, 15 mL), washed twice with aqueous $NaHCO_3$ (1 M, 15 mL) and once with brine (15 mL), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (silica gel, CH_2Cl_2) to afford **12a** as a yellow powder, which was a slight irritant and unstable after several weeks in the fridge. Yield: 690 mg, 93 %; m.p. 126 °C (CH_2Cl_2); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.33$ (s, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 208.0$ (1 C; C=S), 139.4 (2 C; C=C), 20.2 (2 C; CH_2); IR (KBr): $\tilde{\nu} = 1064$ (C=S); 593 cm^{-1} (C–Br); MS (70 eV, EI): m/z (%): 322/320/318 $[M]^{\cdot +}$ (29/48/24), 241/239 (100/85), 165/163 (34/35), 84 (96), 58 (82); elemental analysis calcd (%) for $C_5H_4S_3Br_2$ (320.075): C 18.76, H 1.26, S 30.05, Br 49.93; found C 18.92, H 1.25, S 28.75, Br 50.03.

4,5-Bis(acetylthiomethyl)-2-thioxo-1,3-dithiole (11a): a) Thioacetic acid (1.13 mL, 16.1 mmol) and pyridine (1.32 mL, 16.1 mmol) were added under nitrogen at room temperature to a solution of **12a** (2.34 g, 7.31 mmol) in anhydrous THF (80 mL); this resulted in a brown precipitate. The mixture was stirred for 2 h 30 min and heated under refluxed for an additional hour. After removal of the precipitate by filtration, the solvent was evaporated and purification by column chromatography (silica gel, petroleum ether/CH_2Cl_2 1:1, then CH_2Cl_2) afforded compound **11a** as yellow crystals (2.14 g, 94 %) after recrystallization from EtOAc/petroleum ether.

b) Potassium thioacetate (3.55 g, 31.2 mmol) was added to a solution of **12a** (4.53 g, 14.16 mmol) in anhydrous THF (180 mL) under nitrogen. After this had been heated under reflux for 90 min, the precipitate was removed by filtration. The solvent was evaporated, and purification by column chromatography (silica gel, petroleum ether/CH_2Cl_2 1:1, then CH_2Cl_2) afforded **11a** as yellow crystals after recrystallization from EtOAc/petroleum ether. Yield: 4.00 g, 91 %; m.p. 74 °C ; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.08$ (s, 4 H; CH_2), 2.40 (s, 6 H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 210.4$ (1 C; C=S), 193.6 (2 C; C=O), 138.5 (2 C; C=C), 30.2 (2 C; CH_3), 25.6 (2 C; CH_2); IR (KBr): $\tilde{\nu} = 1699$ (C=O), 1686 (C=O), 1070 cm^{-1} (C=S); MS (70 eV, EI): m/z (%): 310 $[M]^{\cdot +}$ (23), 234 (28), 193 (33), 59 (19), 43 (100); elemental analysis calcd for $C_9H_{10}O_2S_5$ (310.477): C 34.82, H 3.25, S 51.63; found C 34.90, H 3.16, S 51.66.

4,5-Bis(acetylthiomethyl)-2-oxo-1,3-dithiole (11b): a) A solution of **12b**[23] (1.65 g, 5.43 mmol) in anhydrous THF (60 mL) was added to a well-stirred solution of thioacetic acid (0.84 mL, 12 mmol) and pyridine (1 mL, 12 mmol) in anhydrous THF (60 mL). The mixture was heated under reflux under nitrogen. A white precipitate was observed, and heating under reflux was continued for 3 h. The mixture was allowed to cool to room temperature, and the precipitate was removed by filtration. The solvent was evaporated, and purification by column chromatography on silica gel (CH_2Cl_2) afforded compound **11b** as beige crystals (1.57 g, 98 %).

b) A solution of **12b** (140 mg, 0.46 mmol) in anhydrous THF (7.5 mL) was added to a well-stirred solution of potassium thioacetate (116 mg, 1 mmol) in anhydrous THF (7.5 mL), the mixture was heated under reflux under nitrogen. A white precipitate quickly formed, and the resulting brown solution then became darker and darker while heated under reflux for 15 h. After cooling, the solvent was evaporated, and purification by column chromatography on silica gel (petroleum ether/CH_2Cl_2 1:1, then CH_2Cl_2) afforded compound **11b**. Yield: (120 mg, 89 %; m.p. 76 – 77 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.12$ (s, 4 H; CH_2), 2.39 (s, 6 H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 193.8$ (2 C; C=O), 189.8 (1 C; C=O), 127.0 (2 C; C=C), 30.2 (2 C; CH_3), 26.3 (2 C; CH_2); IR (KBr): $\tilde{\nu} = 1682$ (C=O), 1619 cm^{-1} (C=O); MS (70 eV, EI): m/z (%): 294 $[M]^{\cdot +}$ (4), 218 (32), 175 (20), 43 (100); elemental analysis calcd for $C_9H_{10}O_3S_4$ (294.416): C 36.72, H 3.42, S 43.56; found C 36.63, H 3.33, S 43.42.

4,5-(2,3-Dithiabutane-1,4-diyl)-2-thioxo-1,3-dithiole (13a): A solution of **11a** (155 mg, 0.5 mmol) in anhydrous THF (30 mL) was added to a solution of sodium borohydride (127 mg, 3.2 mmol) and anhydrous lithium chloride (16.5 mg, 0.39 mmol) in anhydrous THF (10 mL) under nitrogen. After being heated under reflux for 3 h, the solution was cooled to 0 °C and then quenched with a saturated solution of ammonium chloride (20 mL). The reaction mixture was stirred overnight at room temperature. After extraction with EtOAc, the residue was purified by column chromatography (silica gel, CH_2Cl_2) to afford yellow crystals. Yield: 87 mg, 78 %; m.p. 151 – 152 °C (CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 3.68$ (s, CH_2); MS (EI): 224 $[M]^{\cdot +}$ (100), 160 (60), 96 (11), 84 (24), 69 (13), 58 (30).

4,5-(2,3-Dithiabutane-1,4-diyl)-2-oxo-1,3-dithiole (13b): A solution of MeONa/MeOH prepared from sodium (25 mg, 1.1 mmol) in anhydrous MeOH (2 mL) under nitrogen at room temperature was added to a solution of **11b** (150 mg, 0.51 mmol) in anhydrous MeOH (2 mL). The solution was stirred for 5 min and treated with a solution of iodine (66 mg, 0.26 mmol) in anhydrous Et_2O (2 mL). After an additional 5 min of stirring, the mixture was treated with an NH_4Cl solution (15 mL). The organic layer was extracted twice with EtOAc (10 mL), washed with a $Na_2S_2O_3$ solution (20 mL) and water (20 mL), dried ($MgSO_4$), and evaporated. Purification by filtration on silica gel (petroleum ether/EtOAc 1:1) afforded the disulfide **13b** as an orange oil. Yield: 90 mg, 85 %; ^1H NMR ($CDCl_3$): $\delta = 3.64$ (s, CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 187.1$ (1 C; C=O), 129.7 (2 C; C=C), 29.2 (2 C; CH_2); IR (KBr): $\tilde{\nu} = 1685$ (C=O), 1646 cm^{-1} (C=C); MS (EI): m/z (%): 208 $[M]^{\cdot +}$ (100), 144 (61), 116 (48), 70 (17), 58 (32).

2,3,6,7-Tetrakis(acetylthiomethyl)tetrathiafulvalene (14): a) *Coupling from the dithiolium salt **17***: Triethylamine (2.4 mL, 17.4 mmol) was added at room temperature to a solution of the dithiolium salt **17** (3.19 g, 8.71 mmol) in anhydrous CH_3CN (15 mL) under argon. The resulting colorless solution and brown precipitate were stirred for 1 h. After addition of water (50 mL) and stirring for an additional 1 h, the precipitate was filtered off and washed with water. Purification by a filtration on Florisil (CH_2Cl_2) afforded TTF **14** as orange fibers (1.50 g, 62 %) after recrystallization from THF/petroleum ether.

b) *Substitution of the tetrakis(hydroxymethyl)TTF (**5d**)*: *N,N*-Dimethylformamide diethyl acetal (0.82 mL, 4.8 mmol) and thioacetic acid (0.34 mL, 4.8 mmol) were successively added to a solution of tetrakis(hydroxymethyl)TTF **5d**[11b] (97 mg, 0.30 mmol) in anhydrous THF (25 mL). The reaction mixture was heated under reflux for 48 h under argon. After dilution with CH_2Cl_2 (50 mL), the solution was washed with water (3 × 30 mL), dried ($MgSO_4$), and evaporated. The residue was filtered on Florisil (CH_2Cl_2/EtOAc 4:1), and recrystallization from EtOAc/petroleum ether gave TTF **14**. Yield: 104 mg, 63 %; m.p. 217 °C (THF/petroleum ether); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.92$ (s, 8 H; CH_2), 2.37 (s, 12 H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 194.6$ (4 C; C=O), 128.9 (4 C; C=C), 108.1 (2 C; central C=C), 30.2 (4 C; CH_3), 26.1 (4 C; CH_2); IR (KBr): $\tilde{\nu} = 1688$ cm^{-1} (C=O); MS (70 eV, EI): m/z (%): 556 $[M]^{\cdot +}$ (22), 406 (43), 288 (21), 43 (100); elemental analysis calcd for $C_{18}H_{20}O_4S_8$ (556.834): C 38.83, H 3.62, S 46.06; found C 38.80, H 3.57, S 45.55.

2,3,6,7-Bis(2,3-dithiabutane-1,4-diyl)tetrathiafulvalene (2): A solution of MeONa/MeOH, prepared from sodium (54 mg, 2.38 mmol) in anhydrous MeOH (4 mL) under argon, was added at room temperature to a suspension of compound **14** (300 mg, 0.54 mmol) in anhydrous MeOH/DMF (44 mL, 10:1) and the mixture was heated to 40 °C for 1 h. The orange suspension changed to a red precipitate, which was filtered off and washed with CH_2Cl_2 and EtOAc. Purification by filtration on silica gel (CS_2) afforded SIET (**2**) as a pink powder. Yield: 130 mg, 63 %; m.p. 220 °C; ^1H NMR (200 MHz, $CDCl_3 + CS_2$): $\delta = 3.45$ (s, CH_2); ^{13}C NMR (50 MHz, $C_6D_6 + CS_2$): $\delta = 123.5$ (4 C; C=C); 105.6 (2 C; central C=C); 31.0 (4 C; CH_2); Raman: $\tilde{\nu} = 1542$ (C=C); 511 cm^{-1} (S–S); MS (70 eV, EI): m/z (%): 384 $[M]^{\cdot +}$ (39), 320 (67), 256 (100), 172 (25), 128 (18), 52 (22); elemental analysis calcd for $C_{10}H_8S_8$ (384.655): C 31.22, H 2.10, S 66.68; found C 31.25, H 2.06, S 66.59.

4,5-Bis(acetylthiomethyl)-2-methylsulfanyl-1,3-dithiolium trifluoromethanesulfonate (15): Methyl trifluoromethanesulfonate (1.22 mL, 11.6 mmol) was added at room temperature to a solution of thione **11a** (3 g, 9.68 mmol) in anhydrous CH_2Cl_2 (15 mL) under nitrogen. The resulting dark solution was stirred for 4 h, anhydrous Et_2O (50 mL) was then added, and the solution was left in the fridge overnight. After removal of the ethereal liquid, the resulting oil was dried under vacuum to yield the dithiolium salt **15** as brown crystals. Yield: 4.5 g, 98 %; m.p. 43 – 44 °C (Et_2O); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.47$ (s, 4 H; CH_2), 3.17 (s, 3 H; SCH_3), 2.44 (s, 6 H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 203.2$ (1 C; $CSCH_3$), 194.9 (2 C; C=O), 149.5 (2 C; C=C), 29.9 (2 C; CH_3), 26.1 (2 C; CH_2), 22.9 (1 C; SCH_3); IR (KBr): $\tilde{\nu} = 1693$ cm^{-1} (C=O); MS (FAB): 325 $[M]^+$; elemental analysis calcd for $C_{11}H_{13}O_5S_6F_3$ (474.58): C 27.84, H 2.76; found C 26.94, H 2.68.

4,5-Bis(acetylthiomethyl)-2-methylsulfanyl-1,3-dithiole (16): Sodium borohydride (336 mg, 8.44 mmol) was cautiously added to a solution of the dithiolium salt **15** (4 g, 8.44 mmol) in anhydrous CH_3CN (40 mL) and *i*PrOH (6 mL) under argon at 0 °C. The mixture was allowed to reach room temperature and stirred for 4 h. Purification by column chromatography (silica gel, petroleum ether/EtOAc 8:2) afforded compound **16** as beige crystals. Yield: 2.5 g, 91 %; m.p. 50 °C (EtOAc); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.78$ (s, 1H; CH), 4.02 and 3.87 (2d, $^2J_{\mathrm{AB\,syst.}} = 14.4$ Hz, 4H; CH_2), 2.37 (s, 6H; CH_3), 2.23 (s, 3H; SCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 195.2$ (2C; C=O), 125.0 (2C; C=C), 56.8 (1C; CH), 30.1 (2C; CH_3), 26.5 (2C; CH_2), 11.4 (1C; SCH_3); IR (KBr): $\tilde{\nu} = 1687$ cm^{-1} (C=O); MS (70 eV, EI): *m*/*z* (%): 326 $[M]^{\bullet +}$ (12), 279 (100), 237 (61), 195 (31), 161 (37), 129 (54), 43 (83); elemental analysis calcd for $C_{10}H_{14}O_2S_5$ (326.52): C 36.78, H 4.32; found C 36.80, H 4.31.

4,5-Bis(acetylthiomethyl)-1,3-dithiolium tetrafluoroborate (17): A solution of tetrafluoroboric acid in Et_2O (54 % wt. %, 2.11 mL, 8.4 mmol) was added at 0 °C to a solution of compound **16** (2.5 g, 7.67 mmol) in acetic anhydride (15 mL) under argon. The resulting dark solution was stirred for 1 h. Anhydrous Et_2O (120 mL) was then added, and the solution was left in the fridge overnight. After removal of the ethereal liquid, the resulting oil was dried under vacuum to yield the dithiolium salt **17** as dark crystals. Yield: 2.79 g, 99 %; m.p. 52 °C (Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 11.08$ (s, 1H; CH), 4.57 (s, 4H; CH_2), 2.43 (s, 6H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 195.0$ (1C; CH), 175.8 (2C; C=O), 156.4 (2C; C=C), 30.0 (2C; CH_3), 25.8 (2C; CH_2); IR (KBr): $\tilde{\nu} = 1694$ cm^{-1} (C=O); MS (FAB): 279 $[M]^+$; elemental analysis calcd for $C_9H_{11}O_2S_4F_4B$ (366.25): C 29.51, H 3.03; found C 29.33, H 3.15.

Phosphonium salt 19: Triphenylphosphine (530 mg, 2 mmol) was added at room temperature to a solution of the dithiolium salt **17** (730 mg, 2 mmol) in anhydrous CH_3CN (25 mL) under argon, and the mixture was stirred for 3 h. Anhydrous Et_2O (150 mL) was then added, and the solution was left overnight in the fridge. After removal of the ethereal liquid, the resulting dark oil was dried under vacuum to give the phosphonium salt **19** as a beige mass. Yield: 1.23 g, 98 %; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.37$ (m, 15H; CH arom.), 7.20 (d, $^2J(\mathrm{H,P}) = 4.6$ Hz, 1H; CH), 3.43 and 3.26 (2d, $^2J_{\mathrm{AB\,syst.}} = 14.9$ Hz, 4H; CH_2), 2.30 (s, 6H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 193.9$ (2C; C=O), 135.4–115.5 (CH arom. and C=C), 40.6 (d, $^1J(\mathrm{C,P}) = 42$ Hz, 1C; CH), 30.3 (2C; CH_3), 26.0 (2C; CH_2); IR (KBr): $\tilde{\nu} = 1695$ cm^{-1} (C=O); elemental analysis calcd for $C_{27}H_{26}O_2S_4PF_4B$ (628.52): C 51.59, H 4.17, S 20.41, P 4.93; found C 51.41, H 4.21, S 19.87, P 4.75.

2,3-Bis(acetylthiomethyl)tetrathiafulvalene (10c): a) *Method using the Mitsunobu reaction*: Diethyl azodicarboxylate (0.64 mL, 4 mmol) was added dropwise at 0 °C to a solution of triphenylphosphine (1.05 g, 4 mmol) in anhydrous THF (9 mL) under argon. After this had stirred at 0 °C for 15 min, a solution of 2,3-bis(hydroxymethyl)TTF (**5c**, 0.132 g, 0.5 mmol) and thioacetic acid (0.29 mL, 4 mmol) in anhydrous THF (10 mL) was added dropwise. The resulting dark solution was stirred at 0 °C for 1 h and then at room temperature overnight. The reaction mixture was dissolved in EtOAc (150 mL), washed with brine (3 × 30 mL), and dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 7:3) to afford the TTF **10c** as yellow-ochre crystals (0.097 mg, 51 %) after recrystallization from EtOAc/hexane.

b) *Method using dithiolium salts*: Anhydrous triethylamine (12 mL) was added dropwise over a period of 5 min to a solution of the dithiolium salt **18**[29] (0.570 g, 3 mmol) and the dithiolium salt **17** (1.098 g, 3 mmol) in anhydrous CH_3CN (75 mL) at 0 °C. After stirring at 0 °C for 30 min, the solution was allowed to come up to room temperature over 2.5 h and then concentrated. The residue was dissolved in EtOAc (50 mL) and toluene (50 mL) and the solution was concentrated. The compounds were separated by using chromatography on silica gel [toluene for TTF, toluene/EtOAc (9:1) for dissymmetric TTF **10c**, then toluene/EtOAc (7:3) for tetrakis(thioester)TTF] and were obtained in the following amounts: TTF/**10c**/**14** 0.142 mg, 23 %/0.502 mg, 44 %/0.298 mg, 18 %; this represented an overall yield of 85 %.

c) *Method using dithiolium and phosphonium salts*: Triphenylphosphine (265 mg, 1 mmol) was added under nitrogen to a solution of the dithiolium salt **18**[29] (190 mg, 1 mmol) in anhydrous CH_3CN. After this had stirred for 1 h, the dithiolium salt **17** (365 mg, 1 mmol) in anhydrous CH_3CN (15 mL) was added before dropwise addition of anhydrous triethylamine (1 mL). After the solution had been stirred at room temperature for 30 min it was concentrated. The residue was purified by column chromatography on silica gel [petroleum ether/CH_2Cl_2 (3:7) for TTF, CH_2Cl_2 for dissymmetric TTF **10c**, then CH_2Cl_2/EtOAc (9:1) for tetrakis(thioester)TTF] and the following amounts were obtained: TTF/**10c**/**14** 20 mg, 10 %/237 mg, 63 %/95 mg, 17 %; this represented an overall yield of 90 %. M.p. 90–91 °C (EtOAc/hexane); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.29$ (s, 2H; CH=CH), 3.95 (s, 4H; CH_2), 2.38 (s, 6H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 194.3$ (2C; C=O), 128.5 (2C; C=C), 119.1 (2C; =CH), 30.3 (2C; CH_3), 26.5 (2C; CH_2); MS (EI): *m*/*z* (%): 380 $[M]^{\bullet +}$ (47), 305 (10), 262 (30), 230 (100), 146 (42), 102 (32), 43 (54); elemental analysis calcd for $C_{12}H_{12}O_2S_6$ (380.586): C 37.87, H 3.18, S 50.54; found C 37.90, H 3.12, S 50.01.

2,3-(2,3-Dithiabutane-1,4-diyl)tetrathiafulvalene (3): Sodium borohydride (64 mg, 1.7 mmol) and anhydrous lithium chloride (10 mg, 0.25 mmol) were added to a solution of the bis(thioester)TTF **10c** (95 mg, 0.25 mmol) in anhydrous THF (20 mL) under nitrogen. The solution was heated under reflux overnight, then quenched with a saturated ammonium chloride solution (10 mL). The product was extracted with EtOAc (100 mL), washed with brine (3 × 30 mL), dried ($MgSO_4$), and concentrated. Purification by filtration on Florisil (petroleum ether/EtOAc 4:1) afforded disulfide **3** as orange crystals after recrystallization from EtOAc/petroleum ether. Yield: 20 mg, 28 %; m.p. 174 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.32$ (s, 2H; CH=CH), 3.75 (s, 4H; CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 123.1$ (2C; C=C); 119.1 (2C; =CH); 118.5 (2C; C=C); 111.8 (2C; central C=C); 30.4 (2C; CH_2); MS (EI): *m*/*z* (%): 294 $[M]^{\bullet +}$ (29), 230 (100), 154 (21), 146 (30), 102 (39); elemental analysis calcd for $C_8H_6S_6$ (294.495): C 32.63, H 2.05, S 65.32; found C 32.69, H 2.01, S 65.27; CV (CH_2Cl_2/CH_3CN 9:1, 1.4×10^{-3} M, V vs Ag/AgCl) $Ep_{\mathrm{a1}} = 0.484$, $Ep_{\mathrm{a2}} = 0.944$, $Ep_{\mathrm{c1}} = 0.455$, $Ep_{\mathrm{c2}} = 0.918$, compared with EDT-TTF: (CH_2Cl_2/CH_3CN 9:1, 1.4×10^{-3} M, V vs Ag/AgCl) $Ep_{\mathrm{a1}} = 0.476$, $Ep_{\mathrm{a2}} = 0.907$, $Ep_{\mathrm{c1}} = 0.455$, $Ep_{\mathrm{c2}} = 0.887$.

The following crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 163955–163957:

Salt DIET · $CuBr_4$: $P2_1/n$, $a = 6.639(4)$, $b = 22.113(8)$, $c = 14.015(9)$ Å, $\beta = 99.93(5)°$, $V = 2026(3)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 2.52$ g cm^{-3}, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, 2059 reflections ($2 < \theta < 20°$) were collected at 298 K, 721 with $I > 2\sigma(I)$ used in refinements, 118 refined parameters, $R = 0.059$, $Rw = 0.066$.

(DMTEDT-TTF) · ClO_4: Single crystals of (DMTEDT-TTF) · ClO_4 (1.1 × 0.3 × 0.1 mm) were grown at 4 °C on a platinum-wire anode by oxidation of the donor in a solution of Bu_4NClO_4 (0.1 M in chlorobenzene/EtOH 9:1 at constant low-current density (2 µA cm^{-2}). Triclinic, $P1$, $a = 8.144(3)$, $b = 10.172(2)$, $c = 11.116(2)$ Å, $\alpha = 83.48(1)°$, $\beta = 74.57(2)°$, $\gamma = 86.92(2)°$, $V = 881.6(4)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.831$ g cm^{-3}, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, 5462 reflections ($2 < \theta < 30°$) were collected at 298 K, 3088 with $I > 3\sigma(I)$ used in refinements, 208 refined parameters, $R = 0.061$, $R\mathrm{w} = 0.095$.

(DIET) · ClO_4 · ½ C_6H_5Cl: Single crystals of (DIET) · ClO_4 · ½ C_6H_5Cl (0.6 × 0.3 × 0.1 mm) were grown at 6 °C on a platinum-wire anode by oxidation of the donor in a solution of Bu_4NClO_4 (0.1 M) in chlorobenzene/CH_3CN (8:2) at constant low-current density (1 µA cm^{-2}). Triclinic, P, $a = 9.355(5)$, $b = 10.133(3)$, $c = 11.732(5)$ Å, $\alpha = 105.17(3)°$, $\beta = 99.36(4)°$, $\gamma = 104.92(3)°$, $V = 1005.1(8)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.785$ g cm^{-3}, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, 3741 reflections ($2 < \theta < 25°$) were collected at 298 K, 1803 with $I > 3\sigma(I)$ used in refinements, 262 refined parameters, $R = 0.064$, $R\mathrm{w} = 0.085$.

Acknowledgement

Financial support was provided by the CNRS, MENRT (research studentship to C.D.), and the Ville d'Angers (grant to S.L.M.). We thank Fatia Belarbi for preliminary theoretical calculations on the neutral state of BEDT-TTF and its *S*-position isomers.

---

[1] For recent reviews see: a) J. L. Segura, N. Martín, *Angew. Chem.* **2001**, *113*, 1416–1455; *Angew. Chem. Int. Ed.* **2001**, *40*, 1372–1409; b) M. R. Bryce, *J. Mater. Chem.* **2000**, *10*, 589–598; c) M. B. Nielsen, C. Lomholt, J. Becher, *Chem. Soc. Rev.* **2000**, *29*, 153–164; d) M. R. Bryce, *Adv. Mater.* **1999**, *1*, 11–23; e) J. Becher, J. Lau, P. Mørk, *Electronic Materials*: *The Oligomeric Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**.

[2] a) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M. H. Whangbo, *Organic Superconductors* (*Including Fullerenes*), Prentice Hall, Englewood Cliffs, New Jersey, **1992**; b) *Organic Conductors. Fundamentals and Applications* (Ed.:

J. P. Farges), Marcel Dekker, New York, **1994**; c) H. Mori, *Int. J. Mod. Phys. B* **1994**, *8*, 1–45; d) G. C. Papavassiliou, A. Terzis, P. Delhaes in *Handbook of Organic Conductive Molecules and Polymers, Vol. 1: Charge-Transfer Salts, Fullerenes and Photoconductors* (Ed.: H. S. Nalwa), **1997**, 151–227; e) T. Ishigurao, K. Yamaji, G. Saito, *Organic Superconductors*, 2nd ed., Springer, Berlin, **1998**.

[3] a) A. Krief, *Tetrahedron* **1986**, *42*, 1209–1252; b) G. Schukat, A. M. Richter, E. Fanghänel, *Sulfur Rep.* **1987**, *7*, 155–240; c) M. R. Bryce, *Chem. Soc. Rev.* **1991**, *20*, 355–390; d) G. Schukat, E. Fanghänel, *Sulfur Rep.* **1993**, *14*, 245–390; e) J. Garín, *Adv. Heterocycl. Chem.* **1995**, *62*, 249–304.

[4] At least 20 superconductors made from BEDT-TTF and the following BEDT-TTF kappa phases have been described: κ-(BEDT-TTF)$_2$·Cu(SCN)$_2$ ($T_c = 10.4$ K under ambient pressure), κ-(BEDT-TTF)$_2$·CuN(CN)$_2$Br ($T_c = 11.6$ K under ambient pressure) and κ-(BEDT-TTF)$_2$·CuN(CN)$_2$Cl ($T_c = 12.8$ K, $P = 0.3$ kbar) still hold the record for superconducting transition temperatures in the series: a) H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, J. Tanaka, *Chem. Lett.* **1988**, 53–58; b) A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoot, J. E. Thompson, D. L. Stupka, D. Jung, M. H. Whangbo, *Inorg. Chem.* **1990**, *29*, 2555–2557; c) J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung, M. H. Whangbo, *Inorg. Chem.* **1990**, *29*, 3272–3274; d) J. M. Williams, A. J. Schultz, U. Geiser, K. D. Carlson, A. M. Kini, H. H. Wang, W. K. Kwok, M. H. Whangbo, J. E. Schirber, *Science* **1991**, *252*, 1501–1508; e) J. A. Schlueter, J. M. Williams, U. Geiser, J. D. Dudek, S. A. Sirchio, M. E. Kelly, J. S. Gregar, W. K. Kwok, J. A. Fendrich, J. E. Schirber, W. R. Bayless, D. Naumann, T. Roy, *J. Chem. Soc. Chem. Commun.* **1995**, 1311–1312.

[5] M. R. Bryce, *J. Mater. Chem.* **1995**, *5*, 1481–1496.

[6] a) C. Rovira, J. Veciana, N. Santaló, J. Tarrés, J. Cirujeda, E. Molins, J. Llorca, E. Espinosa, *J. Org. Chem.* **1994**, *59*, 3307–3313; b) J. J. Novoa, M. C. Rovira, C. Rovira, J. Veciana, J. Tarrés, *Adv. Mater.* **1995**, *7*, 233–235; c) E. Ojima, H. Fujiwara, H. Kobayashi, *Adv. Mater.* **1999**, *11*, 758–761; d) E. Ribera, J. Veciana, E. Molins, I. Mata, K. Wurst, C. Rovira, *Eur. J. Org. Chem.* **2000**, 2867–2875.

[7] a) K. Kikuchi, Y. Honda, Y. Ishikawa, K. Saito, I. Ikemoto, K. Murata, H. Anzai, T. Ishiguro, K. Kobayashi, *Solid State Commun.* **1988**, *66*, 405–408; b) G. C. Papavassiliou, G. A. Mousdis, J. S. Zambounis, A. Terzis, A. Hountas, B. Hilti, C. W. Mayer, J. Pfeiffer, *Synth. Met.* **1988**, *27*, B379–383; c) A. M. Kini, M. A. Beno, D. Son, H. H. Wang, K. D. Carlson, L. C. Porter, U. Welp, B. A. Vogt, J. M. Williams, D. Jung, M. Evain, M. H. Whangbo, D. L. Overmyer, J. E. Schirber, *Solid State Commun.* **1989**, *69*, 503–507; d) A. M. Kini, T. Mori, U. Geiser, S. M. Budz, J. M. Williams, *J. Chem. Soc. Chem. Commun.* **1990**, 647–648; e) T. Mori, H. Inokuchi, A. M. Kini, J. M. Williams, *Chem. Lett.* **1990**, 1279–1282.

[8] P. Hudhomme, P. Blanchard, M. Sallé, S. Le Moustarder, A. Riou, M. Jubault, A. Gorgues, G. Duguay, *Angew. Chem.* **1997**, *109*, 896–899; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 878–881.

[9] a) C. Durand, P. Hudhomme, G. Duguay, M. Jubault, A. Gorgues, *Chem. Commun.* **1998**, 361–362.

[10] a) P. Blanchard, M. Sallé, G. Duguay, M. Jubault, A. Gorgues, *Tetrahedron Lett.* **1992**, *33*, 2685–2688; b) P. Blanchard, G. Duguay, J. Garín, J. Orduna, A. Gorgues, M. Sallé, *Rapid Commun. Mass Spectrom.* **1994**, *8*, 701–705; c) P. Blanchard, Doctoral Thesis, Universités de Nantes et Angers (France) **1994**.

[11] a) M. Sallé, A.Gorgues, M. Jubault, K. Boubekeur, P. Batail, *Tetrahedron* **1992**, *48*, 3081–3090; b) M. A. Fox, H.-L. Pan, *J. Org. Chem.* **1994**, *59*, 6519–6527.

[12] We later succeeded in synthesizing the powerful 2,3-bis(bromomethyl)TTF derivatives, which could be transformed into the corresponding thiolesters upon treatment with potassium thioacetate: P. Hudhomme, S. G. Liu, D. Kreher, M. Cariou, A. Gorgues, *Tetrahedron Lett.* **1999**, *40*, 2927–2930.

[13] For reviews see:a) O. Mitsunobu, *Synthesis* **1981**, 1–28; b) D. L. Hughes in *Organic Reactions*, Wiley, New York, **1992**, *42*, 335–656.

[14] a) R. P. Volante, *Tetrahedron Lett.* **1981**, *22*, 3119–3122; b) K. C. Nicolaou, A. L. Smith *Phosphorus Sulfur Silicon* **1993**, *74*, 47–58.

[15] a) K. Lerstrup, I. Johannsen, M. Jorgensen, *Synth. Met.* **1988**, *27*, B9–13, 232; b) V. Y. Khodorkovsky, J. Y. Becker, J. Bernstein, *Synthesis* **1992**, 1071–1072; c) J. S. Zambounis, C. W. Mayer, *Tetrahedron Lett.* **1991**, *32*, 2737–2740; d) T. Nozdryn, J. Cousseau, R. Andreu, M. Sallé, A. Guy, J. Roncali, A. Gorgues, M. Jubault, S. Uriel, J. Orduna, J. Garín, *Synth. Metals* **1995**, *70*, 1159–1160; e) M. Iyoda, H. Suzuki, U. Kux, *Tetrahedron Lett.* **1995**, *36*, 8259–8262.

[16] a) I. Fujii, H. Togame, M. Yamamoto, K. Kanematsu, I. Takayanagi, F. Konno, *Chem. Pharm. Bull.* **1988**, *36*, 6, 2282–2285; b) R. B. Barber, H. Rapoport, *J. Med. Chem.* **1975**, *18*, 11, 1074–1077.

[17] For an overview see: a) G. Capozzi, G. Modena, *The Chemistry of the Thiol Group, Part 1* (Ed.: S. Patai), Wiley, New York, **1974**, 785–839; b) I. V. Koval', *Russ. Chem. Rev.* **1994**, *63*, 9, 735–750; c) K. Ramadas, N. Srinivasan, *Synth. Comm.* **1995**, *25*, 2, 227–234, and references therein.

[18] a) F. Yoneda, K. Suzuki, Y. Nitta, *J. Org. Chem.* **1967**, *32*, 727–729; b) T. Mukaiyama, K. Takahashi, *Tetrahedron Lett.* **1968**, *56*, 5907–5908; c) V. Boekelheide, J. L. Mondt, *Tetrahedron Lett.* **1970**, *14*, 1203–1206.

[19] E. Brzezinska, A. L. Terray, *J. Org. Chem.* **1994**, *59*, 8239–8244.

[20] The oxidation of thiol compounds into the corresponding disulfides has previously been reported to be achievable by use of molecular oxygen as oxidant in the presence of strong bases, aliphatic amines, metal ions, aluminium oxide, or silica gel as catalysts: K.-T. Liu, Y.-C. Tong, *Synthesis*, **1978**, 669–670, and references therein.

[21] This reaction was previously presented in a Poster Communication: “Journée de la Société Française de Chimie”, Piriac-France, 30–31 May **1996**.

[22] P. J. Skabara, K. Müllen, *Synth. Met.* **1997**, *84*, 345–346.

[23] R. M. Renner, G. R. Burns, *Tetrahedron Lett.* **1994**, *35*, 269–272.

[24] a) G. Le Coustumer, Y. Mollier, *J. Chem. Soc. Chem. Commun.* **1980**, 38–39; b) M. Sallé, A. Gorgues, M. Jubault, K. Boubekeur, P. Batail, R. Carlier, *Bull. Soc. Chim. Fr.* **1996**, *133*, 417–426.

[25] An analogous transformation with P(OMe)$_3$ has been observed for thionolactone to afford the corresponding lactone: S. Ayral-Kaloustian, W. C. Agosta, *Synth. Commun.* **1981**, *11*, 1011–1015. We have also witnessed this reaction in other cases, for example: N. Gautier, M. Cariou, A. Gorgues, P. Hudhomme, *Tetrahedron Lett.* **2000**, *41*, 2091–2095.

[26] a) T. L. Gilchrist, J. E. Wood, *J. Chem. Soc. Chem. Commun.* **1992**, 1460–1461; b) T. L. Gilchrist, J. E. Wood, *J. Chem. Soc. Perkin Trans. 1* **1992**, 9–15.

[27] A. J. Parker, N. Kharasch, *Chem. Rev.* **1959**, *59*, 583–628. Triethylphosphite is known to react with diethyl disulfide to yield diethylsulfide and the corresponding ethylthiodiethylphosphonate. See p. 621 (*loc. cit.*) and A. Schönberg, M. Z. Barakat, *J. Chem. Soc.* **1949**, 892.

[28] J. O. Jeppesen, K. Takimiya, N. Thorup, J. Becher, *Synthesis* **1999**, *5*, 803–810.

[29] F. Wudl, P. P. Kaplan, *J. Org. Chem.* **1974**, *39*, 3608–3609.

[30] B. Garreau, D. de Montauzon, P. Cassoux, J. P. Legros, J. M. Fabre, K. Saoud, S. Chakroune, *New J. Chem.* **1995**, *19*, 161–171.

[31] N. C. Gonnella, M. P. Cava, *J. Org. Chem.* **1978**, *43*, 369–370.

[32] A. J. Moore, M. R. Bryce, A. S. Batsanov, J. N. Heaton, C. W. Lehmann, J. A. K. Howard, N. Robertson, A. E. Underhill, I. F. Perepichka, *J. Mater. Chem.* **1998**, *8*, 1541–1550.

[33] J. M. Fabre, L. Giral, A. Gouasmia, H. J. Cristau, Y. Ribeill, *Bull. Soc. Chim. Fr.* **1987**, *5*, 823–826, and references therein.

[34] *Gaussian 98* (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.

[35] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[36] J. P. Lowe, *J. Am. Chem. Soc.* **1980**, *102*, 1262–1269.

[37] Nevertheless, the importance of the electron-withdrawing character could not be clearly demonstrated because the first apparent oxidation potential of EDT-TTF appeared to be more positive than that corresponding to its *S*-position isomer **3**.

[38] V. Khodorkovsky, A. Edzifna, O. Neilands, *J. Mol. Electron.* **1989**, *5*, 33–36.

[39] M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439–4449.

[40] a) M. E. Kozlov, Y. Tanaka, M. Tokumoto, T. Tani, *Chem. Phys. Lett.* **1994**, *223*, 318–322; b) M. E. Kozlov, Y. Tanaka, M. Tokumoto, T. Tani, *Synth. Met.* **1995**, *70*, 987–988.

[41] K. Zimmer, B. Gödicke, M. Hoppmeier, H. Meyer, A. Schweig, *Chem. Phys.* **1999**, *248*, 263–271.

[42] K. A. Abboud, M. B. Clevenger, G. F. de Oliveira, D. R. Talham, *J. Chem. Soc. Chem. Commun.* **1993**, 1560–1562; b) L.-K. Chou, M. A. Quijada, M. B. Clevenger, G. F. de Oliveira, K. A. Abboud, D. B. Tanner, D. R. Talham, *Chem. Mater.* **1995**, *7*, 530–534.

[43] S. Le Moustarder, Doctoral Thesis, Université d'Angers (France) **1998**.

[44] a) S. Le Moustarder, P. Hudhomme, M. Sallé, P. Blanchard, A. Riou, M. Jubault, G. Duguay, A. Gorgues, *Synth. Met.* **1998**, *94*, 41–44; b) S. Le Moustarder, N. Mercier, P. Hudhomme, A. Gorgues, A. Riou, *Synth. Met.* **1999**, *102*, 1671–1672; c) S. Le Moustarder, P. Hudhomme, C. Durand, N. Mercier, M. T. Azcondo, P. Delhaes, A. Riou, A. Gorgues, *J. Mater. Chem.* **2000**, *10*, 617–623; d) S. Le Moustarder, P. Hudhomme, B. Illien, J. F. Halet, A. Gorgues, A. Riou, *Mol. Cryst. Liq. Cryst.* **2000**, *338*, 61–74.

[45] K. A. Abboud, L.-K. Chou, M. B. Clevenger, G. F. de Oliveira, D. R. Talham, *Acta Cryst. Section C* **1995**, 2356–2362.

[46] B. A. Scott, S. J. L. Placa, J. B. Torrance, B. D. Silverman, B. Welber, *J. Am. Chem. Soc.* **1977**, *99*, 6631–6639.

[47] TM-TPDS corresponds to 2-[4,5-bis(methylthio)-1,3-diselenol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene: Y. Misaki, T. Kaibuki, M. Taniguchi, K. Tanaka, T. Kawamoto, T. Mori, T. Nakamura, *Chem. Lett.* **2000**, 1274–1275.

[48] H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, G. Saito, T. Enoki, H. Inokuchi, *Chem. Lett.* **1984**, 179–182.

Received: May 25, 2001 [F3287]