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Trithiaazafulvalene: A Promising Building Block between Tetrathiafulvalene and Dithiadiazafulvalene

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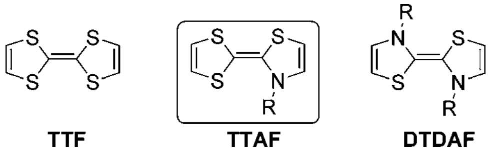
ABSTRACT



New electroactive building blocks, the trithiaazafulvalenes (TTAFs), were synthesized. These redox-active molecules, intermediate between tetrathiafulvalene (TTF) and dithiadiazafulvalene (DTDAF), show promising features for the elaboration of molecular materials.

Intensive unabated studies have focused on the tetrathiafulvalene (TTF) derivatives for the preparation of molecular conductors for the last 30 years.[1] Several modifications of the TTF moiety have been performed either to achieve better conductivity properties or to understand structure−activity relationships. Among them, the replacement of two sulfur atoms in the TTF framework by nitrogen atoms leads to the dithiadiazafulvalenes (DTDAFs).[2] Compared with TTFs, DTDAFs exhibit higher electron-donating properties but an instability upon air exposure leading to various oxidative rearrangements.[3] An interesting aspect of DTDAF chemistry is the possibility to modify the R substituents on the nitrogen atoms, for example, to obtain the cis isomer by connecting the two thiazole cores by a N,N′-bridge or to use the R substituent as a handle for further functionalization.[2] As all the DTDAFs, even those substituted with electron-withdrawing groups,[4] seem labile to oxygen, we decided to investigate the synthesis of trithiaazafulvalene (TTAF) which should exhibit intermediate properties between the DTDAF the TTF derivatives and show the best features of each family, that is, the excellent electron-donating properties of DTDAF and the stability of TTF. The first TTAF was reported 30 years ago from the reaction of 3-methylbenzothiazolium salt with 2-piperidino-1,3-benzodithiole affording a benzoannelated TTAF.[5] Ten years later, 3-methylbenzothiazolium salt was also used in cross reactions with non-benzoannelated dithiole, but none of these publications reported investigations on the redox properties or the structural conformations of these trithiazafulvalenes (TTAF).[6] Benzoannelated derivatives of TTF or DTDAF are usually easier to prepare and are more stable as they exhibit higher oxidation potentials but are less attractive as precursors of molecular materials than the corresponding non-benzoannelated donor cores.[1] Herein, we report the synthesis and the structural and electrochemical properties of non-benzoannelated TTAF using 4,5-dimethyl-2-piperidino-1,3-dithiole and various substituted thiazolium

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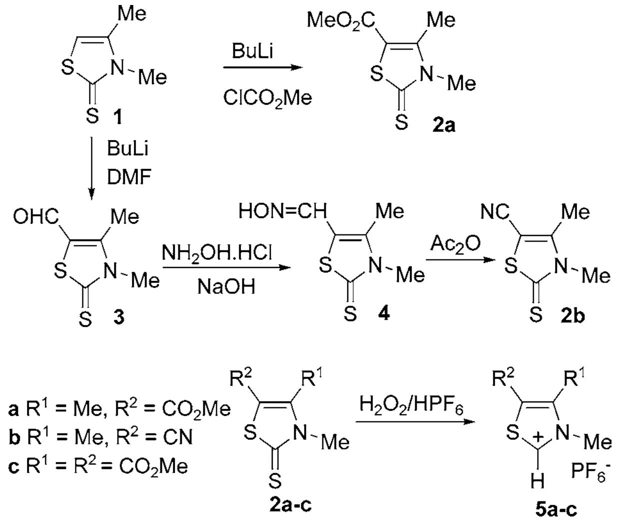
cores. At least one electron-withdrawing group on the thiazole core was included to moderate the strength of the electron-donating ability, and eventually, their lability toward oxygen will enable us to compare them with the parent donors.

The approach we chose for the synthesis of our target precursors, the thiazolium salts, is outlined in Scheme 1.

Scheme 1. Synthesis of the Target Precursors

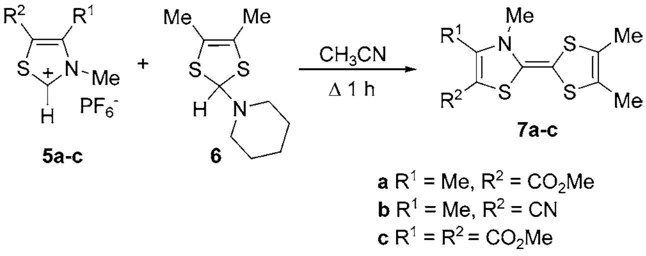


Lithiation of heterocycles is a very useful route for the preparation of various substituted derivatives.[7] Metalation of the 1,3-thiazoline-2-thione ring on the 5 position can be realized using strong bases such as BuLi or lithium diisopropylamide (LDA) and the lithiated species can then react with a variety of electrophiles.[8]

For our purpose, we use in this reaction the 3,4-dimethyl-1,3-thiazoline-2-thione **1**[9] that we lithiated with BuLi and then reacted with either methyl chloroformate or dimethyl formamide as the electrophile to give the monoester **2a** or the aldehyde **3**. The conversion of the aldehyde **3** into the corresponding nitrile **2b** was realized through the dehydration of the intermediate aldoxime **4**. First, the thiazole-2-thione aldehyde **3** was heated in the presence of hydroxylamine hydrochloride to afford the aldoxime **4** which can be either isolated (90% yield) or directly transformed into the nitrile by simply heating with acetic anhydride. The resulting nitrile **2b** is obtained with an overall yield of 72%. Thiazoline-2-thiones **2a** and **2b** were converted to the corresponding thiazolium salts **5a**,**b** with hexafluorophosphoric acid and hydrogen peroxide.[10] We also synthesized thiazolium salt **5c** from 1,3-thiazoline-2-thione **2c** ($R^1 = R^2 = CO_2Me$) substituted with two electron-withdrawing groups according to the procedure described above.[4] Having these thiazolium salts in hand, we prepared the 4,5-dimethyl-2-piperidino-1,3-dithiole **6** for the cross-coupling experiment according to literature procedure.[11]

On the basis of the experiments carried out previously for the synthesis of benzoannelated TTAF, the thiazolium salts **5** were heated to reflux in acetonitrile with 1 equiv of 2-piperidino-1,3-dithiole **6** (Scheme 2). After 1 h at reflux, the TTAFs **7a**−**c** precipitated from the solution and were isolated by filtration. It is noteworthy that these derivatives can be purified by recrystallization and stored under ambient conditions for months without alteration.

Scheme 2. Synthesis of TTAFs



Single crystals were obtained for **7a** and **7b**, and the X-ray molecular structures are given in Figure 1. Both TTAFs present similar trends such as a fully planar donor core, a head to tail organization of two neighboring TTAFs, and formation of stacks (see Supporting Information). The shortest intermolecular S···S distances are equal to 3.860(17) and 3.995(6), respectively, for **7a** and **7b**. The bond lengths in the TTAFs **7a** and **7b** are collected in Table 1 together with those of the tetramethyl TTF (TMTTF)[12] and the hexamethyl DTDAF.[13] Comparison of these bond lengths

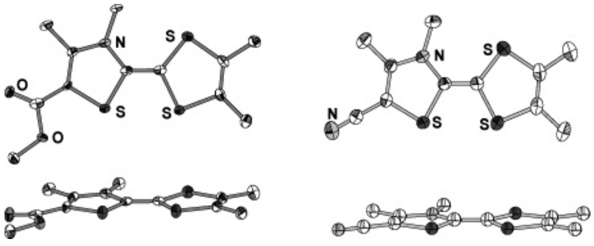


Figure 1. X-ray crystal structure of **7a** (left) and **7b** (right) (CCDC 602405−602406). The displacement ellipsoids are drawn at the 50% probability level.

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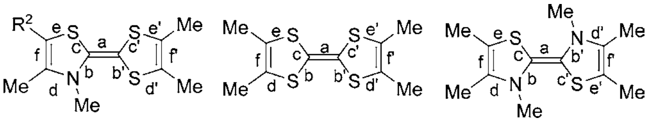
Table 1. Bond Lengths (Å) for TTAFs **7a**, **7b**, TMTTF, and DTDAF

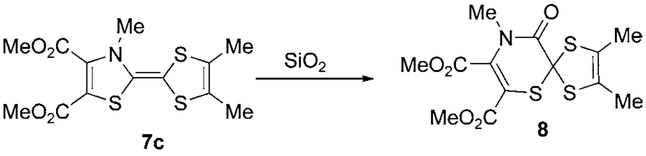


	7a	**7b**	DTDAF	TTF
a	1.360(9)	1.346(4)	1.341(2)	1.359(2)
b	1.418(8)	1.406(3)	1.438(2)	
b′	1.747(13)	1.760(4)	1.392(2)	1.764(2)
c	1.754(13)	1.763(3)	1.779(2)	
c′	1.773(7)	1.762(4)	1.762(2)	1.761(3)
d	1.37(1)	1.364(5)	1.397(2)	
d′	1.757(10)	1.750(2)	1.432(2)	1.765(3)
e	1.769(10)	1.758(2)	1.764(2)	
e′	1.771(12)	1.395(4)	1.769(2)	1.769(2)
f	1.362(8)	1.326(4)	1.339(2)	
f′	1.336(8)	1.317(4)	1.329(2)	1.343(2)

is instructive. As can be seen in Table 1, each heterocycle in TTAF maintains its characteristic bond lengths. The thiazole core and the dithiole core of the TTAFs are comparable to that of the DTDAF and the TTF, respectively, as well as the central C═C bonds.

Interestingly, we also tried to purify by column chromatography the derivative **7c**. In this case, ^{1}H NMR and ^{13}C NMR data and X-ray crystal structure determination proved this compound to be a novel oxygen-containing product, the spiroamide **8** (Scheme 3 and Figure 2).

Scheme 3. Oxidation on Silica Gel of DTDAF **7c**



The behavior of **7c** parallels that of DTDAFs which upon air exposure are easily oxidized and converted into such spiro amide derivatives or a 10-membered ring compound.[3]

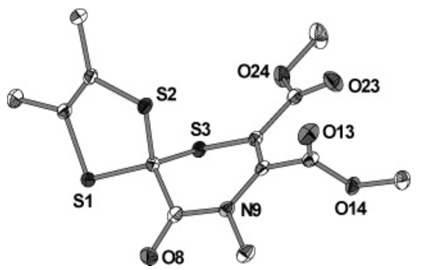


Figure 2. X-ray structure of the spiroamide **8** (CCDC 602407). The displacement ellipsoids are drawn at the 50% probability level.

However, the trithiaazafulvalenes described here suffer from this drawback only upon chromatography whereas they are stable for months in the solid state, a striking difference from the DTDAF.

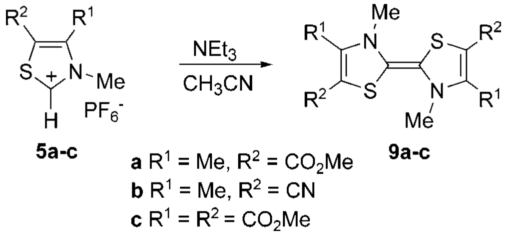
To get information on the redox properties of these new donors, we performed cyclic voltammetry experiments. The oxidation potentials of TTAFs **7a**−**c** are listed in Table 2 together with those of the parent donors DTDAFs **9a**−**c** and TMTTF for comparison. For that purpose, we prepared the corresponding DTDAFs **9a**−**c** directly from thiazolium salts **5** (Scheme 4).

Table 2. Oxidation Potentials in V vs SCE for TMTTF, **7a**−**c**, and **9a**−**c**[a]

	R^1	R^2	E^1	E^2	ΔE (mV)
TMTTF			0.23	0.59	360
7a	Me	CO_2Me	−0.04	0.35	390
9a	Me	CO_2Me	−0.33	−0.09	240
7b	Me	CN	0.04	0.40	360
9b	Me	CN	−0.09	0.12	210
7c	CO_2Me	CO_2Me	0.12	0.48	360
9c	CO_2Me	CO_2Me	−0.08	0.15	230

[a] Pt working electrode with 0.1 M Bu_4NPF_6 in CH_3CN has a scan rate of 100 mV/s.

Scheme 4. Synthesis of DTDAF **9**



a R^1 = Me, R^2 = CO_2Me
b R^1 = Me, R^2 = CN
c R^1 = R^2 = CO_2Me

The base-catalyzed deprotonation of the thiazolium salts was realized in acetonitrile using triethylamine under an inert atmosphere. After 20 min, the DTDAFs formed in the medium precipitate were quickly filtered off and directly electrochemically analyzed without isolation because of the strong air sensitivity mentioned above.

For all the donors, two monoelectronic reversible processes were detected indicating that each donor possesses three redox states: neutral, cation radical, and dication. Redox potentials of the TTAFs are intermediate between those of the TTF and DTDAF donors. Interestingly, one can notice the larger potential difference between the two oxidation waves ($\Delta E = E^2 - E^1$) of TTAFs **7a**−**c** when compared to DTDAFs **9a**−**c**, which indicates that for TTAF the cation radical species is stable in a wider potential window than that for DTDAF. Actually, these ΔE values for **7** are comparable with the one observed for TMTTF.

DFT calculations [B3LYP/6-31G(d)] were performed on the unsubstituted model derivatives, the *N*-methyl-TTAF, the

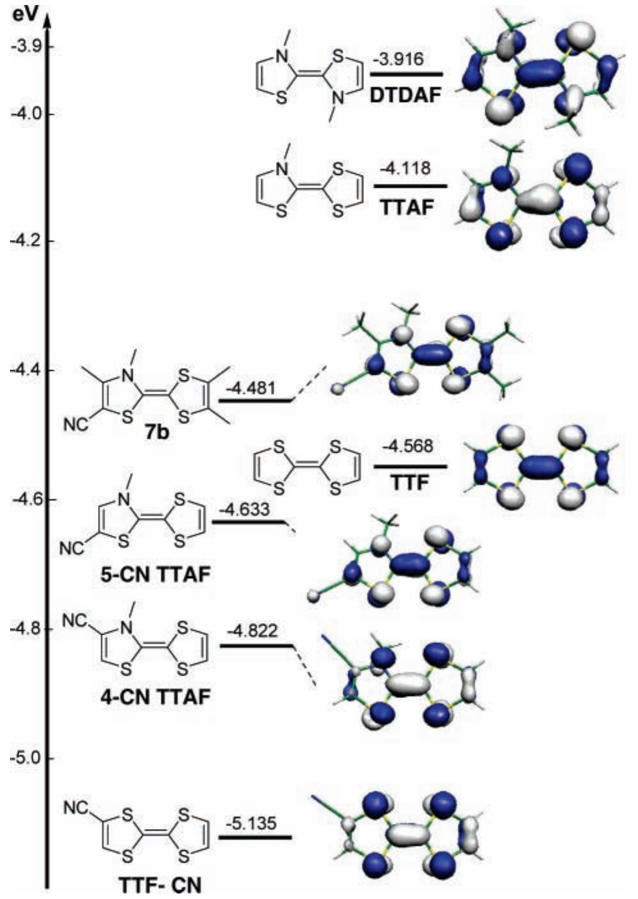


Figure 3. Molecular orbital surfaces and HOMO levels of unsubstituted TTF, TTAF, DTDAF, monocyano TTF and TTAF, and **7b**.

N,*N*′-dimethyl-DTDAF, and the TTF, to determine the evolution of their HOMO energies as well as their shape. As shown in Figure 3, the energy of the HOMO of TTAF is indeed located between those of TTF and DTDAF but is closer in energy to the DTDAF system. Note also the very small coefficient at the C4 carbon atom of the thiazole ring, located α to the NMe group. This evolution of the HOMOs was anticipated from our experience in the electrochemistry of the symmetrical DTDAF molecules,[2] hence the functionalization of the TTAF core with electron-withdrawing groups (−CN, $-CO_2Me$) described above. The same calculations were therefore performed with −CN substituted donor molecules. Indeed, the HOMO of TTF is stabilized by 0.567 eV in TTF−CN. Concerning the TTAF, in that case, two position isomers can be considered, with the CN group on the C4 (close to the NMe group) or the C5 carbon atom of the thiazole ring. A sizable difference is observed between the two isomers, and the HOMO of the C4-substituted isomer is more strongly stabilized than that of the C5-substituted isomer. The stabilizing effect of the CN can also be partially counterbalanced by the four methyl groups as shown in Figure 3 for the **7b** derivative discussed above. In these cases, a strong stabilization of the HOMO of the TTAF is obtained, which brings these molecules to energy levels comparable to that of TTF itself.

In summary, we have shown that TTAF is a novel class of electron-donor molecules whose electronic properties and stability compare with those of TTF, provided that an electron-withdrawing group is introduced on the thiazole ring. Further investigations will be devoted to the elaboration, either chemically or electrochemically, of ion radical salts with these TTAF derivatives.

Supporting Information Available: Experimental conditions and characterization data for compounds **7** and **8**, details of calculations, and X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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