Dithiadiazafulvalenes: Promising Precursors of Molecular Materials

D. Lorcy* and N. Bellec

Groupe Hétérochimie et Matériaux Electroactifs, Institut de Chimie de Rennes, UMR-CNRS 6510-Université de Rennes 1, Campus de Beaulieu, Bât 10A, 35042 Rennes Cedex, France

Contents

Dominique Lorcy was born in Lorient (France) in 1963. She received her Ph.D. degree in Organic Chemistry in 1991 from the University of Rennes 1 under the supervision of Professor A. Robert. She was a postdoctoral fellow from 1991 to 1992 with Professor M. P. Cava at the University of Alabama at Tuscaloosa developing the synthesis of copolymers based on thiophene. In 1992, she returned to the University of Rennes 1, became a Maître de Conférences, and was promoted Professor in 1999. Her current research interests are in the area of heterocyclic chemistry of electroactive derivatives, electrochemical synthesis, chemistry of molecular materials, and, recently, hybrid organic–inorganic building blocks.

Nathalie Bellec was born in Vannes (Morbihan, France) in 1972. She received her Ph.D. degree in Organic Chemistry in 1998 from the University of Rennes (France). She was awarded the Slovenian Krka prize for her research on organic materials based on dithiadiazafulvalenes. After a postdoctoral position on the synthesis of new porphyrazines at Imperial College (London) in Professor A. G. M. Barrett's laboratory, she joined the faculty at the University of Rennes as a Maître de Conférences in 2000. Her present research interests include the synthesis and characterization of novel functionnalized TTF and the preparation of hybrid materials via coordination or sol–gel chemistry.

## 1. Introduction

1.1. Background

One of the most astonishing electrical phenomena discovered during the last three decades of the 20th century is the metallic conductivity observed in an organic complex resulting from the association and the interactions of two components: as electron donor, the tetrathiafulvalene (TTF), and as electron acceptor, the tetracyanoquinodimethane (TCNQ).[1] The discovery of this one-dimensional metallic conductivity in 1973 provided the impetus for unabated international research activity aimed at the modification of donor and acceptor moieties to achieve better conductivity properties and to understand the structure–activity relationships. Concerning the donor, research efforts were placed into the replacement of some or all of the sulfur atoms in the fulvalene framework by more polarizable atoms.[2–4] For instance, the first organic superconductors at low temperature are the Bechgaard salts based on the tetramethyltetraselenafulvalene (TMTSF).[5]

* To whom correspondence should be addressed. Tel: 33 2 23 23 62 73. Fax: 33 2 23 23 67 38. E-mail: Dominique.lorcy@univ-rennes1.fr.

TTF   TMTSF

BEDT-TTF   dibenzo-DTDAF
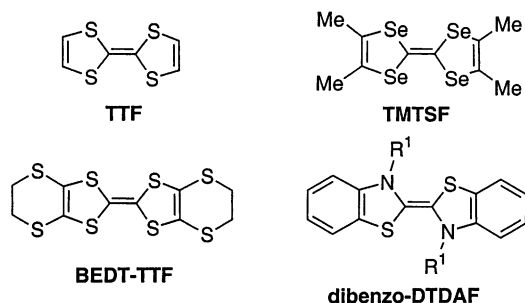
Further efforts to achieve a superconducting state at higher temperatures were oriented toward functionalization of the TTF framework, which could increase interactions between the donors in the solid state.[2–4,6] This resulted in the design and synthesis of heterocycle-fused TTF such as bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF).[7] Several other modifications were realized; among them, the replacement of two sulfur atoms in the TTF framework by nitrogen ones led to the dithiadiazafulvalenes (DTDAF). Actually, this type of donor, first called bis-thiazolylidenes, appeared 40 years ago in the literature in the search for "isolable, stable" carbenes.[8–11] Also, from a biological point of view, it is noteworthy that these carbenes (thiazole-2-ylidenes) and their dimers (DTDAF) have received considerable attention as potential catalytic species in the chemistry of vitamin B_1 such as the benzoin condensation.[12–23] Back to the molecular materials field, in 1976, Wheland and Gillson reported over 80 electrically conductive charge transfer complexes based on various donor and acceptor molecular structures.[24] Among them, the bis(3-methyl benzo-1,3-thiazolylidene) or dibenzo-DTDAF, in the presence of TCNQ and 2,5-dimethoxy TCNQ, exhibited low resistivities on compressed pellets (respectively, 20 and 30 Ω cm). Nevertheless, as compared to the extensive studies carried out on TTF derivatives during the last 30 years, DTDAFs have only been scarcely studied as precursors of organic materials. The discovery that dibenzo-DTDAF is oxygen sensitive[9,25,26] has slowed further research in the field of new DTDAF donors and thwarted their use as precursors of organic materials. Thus, dibenzo-DTDAF stayed the only representative of this family that was employed in charge transfer complexes formation for a long time. DTDAFs have regained interest as precursors of organic materials in the past decade. The DTDAFs are striking derivatives, which start their lives accidentally from the carbene chemistry, act as a catalytic species into acyloin transformation, and begin new lives as precursors of organic materials.

1.2. A Side Product of Carbene Chemistry

During the course of their studies on carbenes possessing quasi-aromatic resonance stabilization, Wanzlick et al.[8] observed that benzothiazolium salts 1-R^1 treated with tertiary amines such as triethylamine yield a carbene 2-R^1, which dimerizes more or less readily into the ethylene derivative 3-R^1 (Scheme 1). This first report on the unexpected formation of DTDAFs was realized in 1964.[8] Almost

simultaneously, Vorsanger characterized this dimer 3-R^1, first called bis(benzo-1,3-thiazolyline-2-ylidene), as a compound very sensitive to air, which formed various oxidation products (vide infra).[9] Further studies were devoted to the isolation of nucleophilic carbenes from benzothiazolium salts, but only the dimers 3-R^1, the corresponding benzoannelated DTDAFs, were isolated.[10,11,27–29]

Scheme 1

1-R^1 2-R^1 ylide   2-R^1 carbene

3-R^1
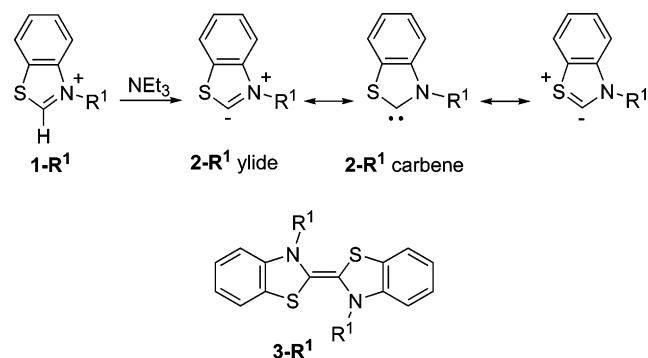
It was only three decades later that Arduengo et al., taking advantage of steric effects, found the right substituent on the nitrogen atom, which enabled them to isolate a stable thiazol-2-ylidene.[30] They generated the thiazole carbene by treating 3-(2,6-diisopropylphenyl)-4,5-dimethyl thiazolium chloride (4-Dipp) with potassium hydride at room temperature under dry nitrogen (Scheme 2). This carbene 5-Dipp can be stored in the absence of oxygen and moisture and was structurally characterized.

Scheme 2

4-Dipp   5-Dipp

Dipp = 2,6-diisopropylphenyl
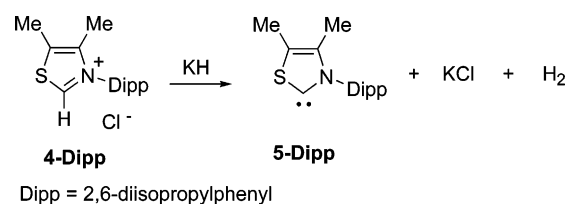
1.3. Catalytic Species into Acyloin Condensation

DTDAFs and thiazolium salts have also been studied to elucidate the role of thiamin into the biochemical reaction mechanism. Thiamin or vitamin
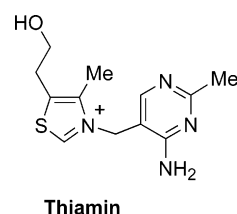
Thiamin

B_1, in the form of its diphosphate resulting from the reaction of thiamin with ATP, serves a number of essential metabolic functions including the decarboxylation of pyruvic acid to acetaldehyde and the conversion of pyruvic acid to acetoin.[12] According to his study on model systems, Breslow proposed a mechanism where the thiazolin-2-ylidene, generated by dissociation of the proton from the C-2 of the

Scheme 3
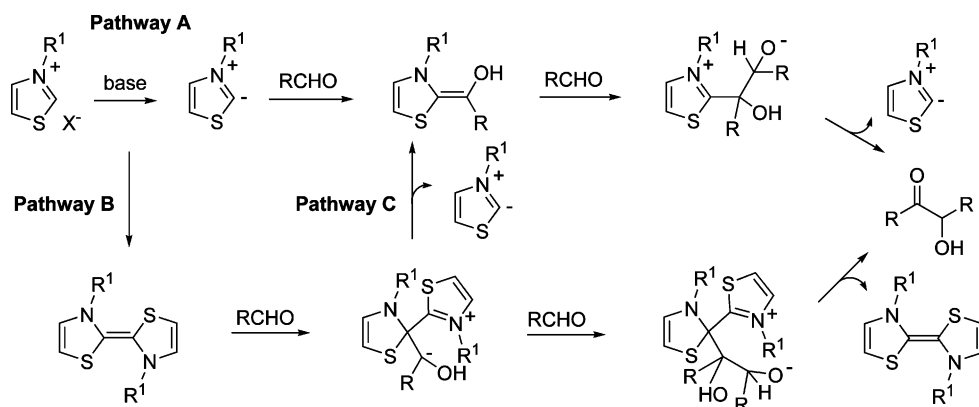
thiazolium ring, is the catalytic species involved in these types of reactions.[13] The catalysis by the thiamine ylide in the benzoin type condensation reactions of aldehydes leading to α-ketols occurs in a fashion analogous to catalysis by cyanide ion. According to kinetic studies in mild basic conditions, the reaction is first order in thiazolium ion (pathway A, Scheme 3).[14] However, as thiazolin-2-ylidene can also react with thiazolium salt to form the bis-(thiazolin-2-ylidene) in aprotic media, benzoin condensations have also been claimed to be catalyzed by this dimer.[15−22] For instance, Lopez-Calahorra et al. have reported several experimental evidences that in an aprotic medium the actual catalytic species is the bis(thiazolin-2-ylidene) according to pathway B in Scheme 3.[18]

Another mechanism involving the dimer was also proposed according to the Lemal mechanism,[31] in the description of the reaction between tetraaminoethylene and electrophiles, showing that carbenelike reactions could proceed directly from olefins, the dimer of the carbenes.[22] Myles et al. used thiazolium-functionalized self-assembled monolayers (SAMs) to investigate the mechanism of the thiazolium-promoted acyloin condensation.[23] They found out that the mechanism occurs as decribed in pathway C (Scheme 3) confirming the role of the dimer, or DTDAF, as a competent intermediate for the acyloin transformation.

In this review, we will concentrate on DTDAFs as precursors of organic materials. The various approaches used to form the DTDAF core and their reactivity toward oxygen are presented. Correlation of the electrochemical behavior with the molecular geometry of the donor core is analyzed together with the charge transfer salts in which the DTDAFs are embedded.

2. Syntheses of DTDAFs

Two main strategies were applied to form the DTDAF framework: either via chemical and/or electrochemical coupling of various thiazole cores (routes A, B, and C) or via the alkylation of the preformed 2,2′-bithiazole followed by reduction of the corresponding bithiazolium salt (route D) as depicted in Scheme 4. Note that routes A−C were used to prepare DTDAFs not only resulting from an intermolecular coupling of the various thiazole cores but

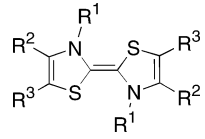also from an intramolecular coupling to afford N,N′-bridged DTDAFs, with a large variety of substituents.

Scheme 4
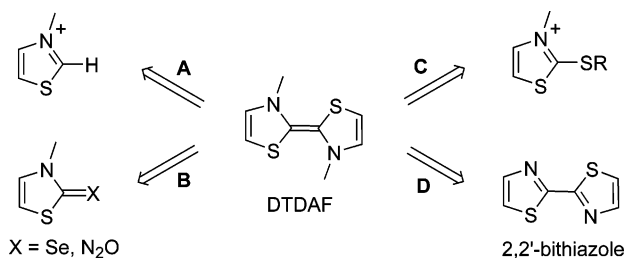
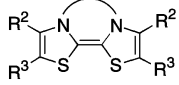The following discussion describes the various approaches to DTDAF, which are collected in Tables 1−3.

Table 1. Routes to Benzannelated DTDAF
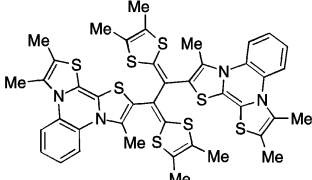
R^1	X	Route	Ref.
Me	H	A	9, 10, 25, 29
		B	47, 55
		D	58
Et	H	A	25, 34, 36, 40
Et	OMe	A	34, 36
Et	Cl	A	34, 36
Et	CO_2Et	A	34, 36
Et	NO_2	A	34, 36
CH_2Ph	H	A	35
CH_2Ph	Me	A	35
Ph	H	B	47
p-$NO_2C_6H_4CH_2$	H	A	33
		B	47
		A	15, 25, 27

Table 2. Routes to Nonbenzannelated DTDAF

R^1	R^2	R^3	route	ref
Me	Me	Me	A	30
			B	52
Me	Me	H	A	38
Me	H	H	D	61
Me	Me	COMe	B, C	52, 53
Me	Me	CO_2Et	A	37
			B	54
			B, C	52, 53
Me	CO_2Me	CO_2Me	B	49, 50
Me	CN	CN	B	49, 50
Et	Me	H	A	38
Et	Me	$(CH_2)_2OH$	A	38
CH_2Ph	Me	H	A	38
CH_2Ph	Me	$(CH_2)_2OH$	A	38
CH_2CO_2Et	Me	CO_2Et	B	54
Ph	SMe	CO_2Me	B	48, 50
Ph	CO_2Me	CO_2Me	B	49, 50
Ph	Me	COMe	B, C	53
Ph	Me	$CMedC(CN)_2$	B, C	53
Ph	SMe	$p\text{-}ClC_6H_4$	A	39
$p\text{-}NO_2C_6H_4$	SMe	$p\text{-}ClC_6H_4$	A	39
2,6-Dipp[a]	Me	Me	A	30
2,4,6-Mes[b]	Me	Me	A	30

[a] 2,6-Dipp = 2,6-diisopropylphenyl. [b] 2,4,6-Mes = 2,4,6-trimethylphenyl.

Table 3. Routes to N,N′-Bridged DTDAF

| N,N′-bridge	R^2	R^3	Route	Ref.
(o-phenylene)	Me	Me	B, C	51
			C	56
	Me	CO_2Et	C	56
(dioxa bridge)	Me	Me	A, B	42
	Me	H	A, B	42
	H	H	A, B	42
	Me	CO_2Et	A, B	42
	Me	COMe	A, B	42
$(CH_2)_n$ n=2-4	H	H	A, C	41
			D	61
$(CH_2)_n$ n=2-8	Me	Me	A	18
			A, C	41
$(CH_2)_2$	Me	H	A, C	41
$(CH_2)_2$	Me	COMe	A, C	41
$(CH_2)_2$	Me	CO_2Et	A, C	41
$(CH_2)_n$ n=2-8	-CH=CH-CH=CH-		A	18
			B	55
			D	58
(bis-thiazole structure)			C	56

2.1. Coupling of 1,3-Thiazolium Salts in Basic Medium (Route A)

The first precursors used by several groups in the synthesis of DTDAF were the 1,3-thiazolium salts. As mentioned above, these salts in aprotic media and in the presence of base afford the dimer called bis-(1,3-thiazolin-ylidene) or DTDAF (Scheme 5). It is

Scheme 5
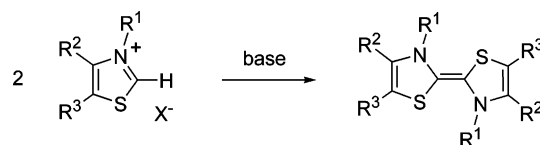
worth noting that in some conditions the ring opening of thiazole core is also observed instead of the coupling.[32,33] This synthetic strategy is one of the most employed pathways towards DTDAF and gives rise to various substituted donor derivatives (Tables 1−3).[15,18,25,27,29,30,33−42]

Two mechanisms were first proposed to explain the formation of the benzoannelated-DTDAF **3**-R^1 core from the reaction of benzothiazolium **1**-R^1 with triethylamine (Scheme 6):[10,25] either a direct reaction of two carbenes **2**-R^1 (pathway A, Scheme 6) or an indirect reaction where the carbene **2**-R^1 reacts with the thiazolium salt **1**-R^1 followed by a deprotonation of the intermediate to yield the ethylenic dimer (pathway B, Scheme 6). Early ^{1}H NMR experiments carried out on this dimer indicate that in solution, it exists under the two isomeric forms (cis/trans).[28,43,44]

Scheme 6

Pathway A

Pathway B
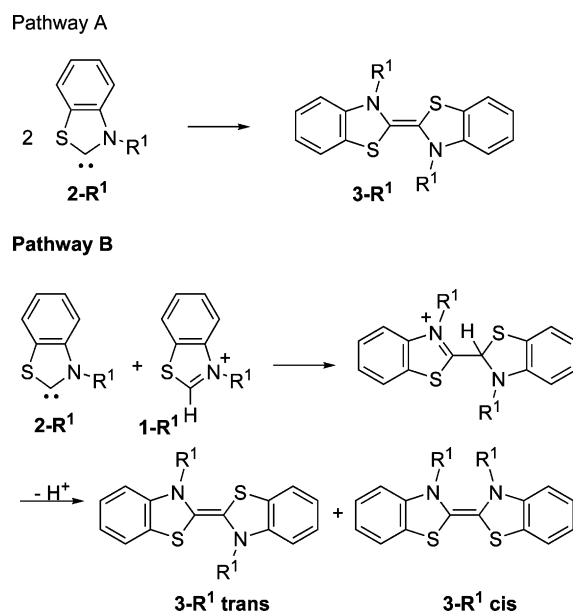

Doughty and Risinger extended their study to nonbenzoannelated thiazolium salts such as the electron deficient 5-ethoxycarbonyl 3,4-dimethylthiazolium salt **6**-Me and related thiazolium salts, which led to the dimers in basic medium (Scheme 7).[37] On the basis of their experiments, they concluded that the thiazolyl carbenes were dimerizing through a direct mechanism.

Scheme 7

**6-R^1**   **7-R^1**
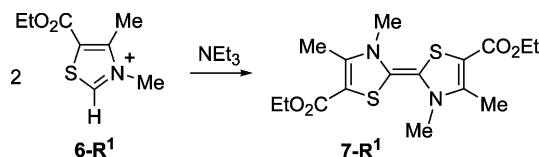
However, and as pointed out by Washabaugh and Jencks, an ionic mechanism involving the ylide addition to the thiazolium salt was not ruled out.[45] Experimental evidences were brought by Bordwell and Satish,[38] who studied the acidities of C2 hydrogen atoms in various thiazolium cations and the reactivity of their conjugated bases toward nucleophilic addition of the ylide to the thiazolium salt C2 position. They also investigated the redox behavior of thiazolium salts in dimethyl sulfoxide in basic medium and performed cross-over experiments with two different thiazolium salts. This indirect mechanism in aprotic solvents, involving the nucleophilic addition followed by deprotonation (Scheme 8), was confirmed by Jordan et al. using ^{13}C NMR investigations on cross-over experiments involving thiazolium-2-d salt and [2-^{13}C]thiazolium salt.[46]

Scheme 8
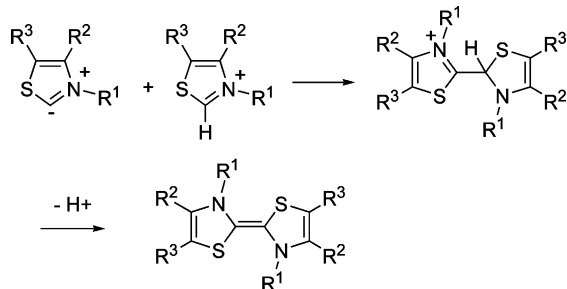
These findings were also supported by Arduengo et al. who observed that dimerization of the isolated carbene proceeds only in the presence of trace amounts of acid while in the absence of such catalyst no dimerization occurs on a time scale of weeks (Scheme 9).[30] They showed that not only the carbene **5**-Dipp could be isolated and crystallographically characterized but its dimer **8**-Dipp could be isolated and crystallographically characterized as well.

Scheme 9

5-Dipp   **8-Dipp**

Dipp = 2,6-diisopropylphenyl
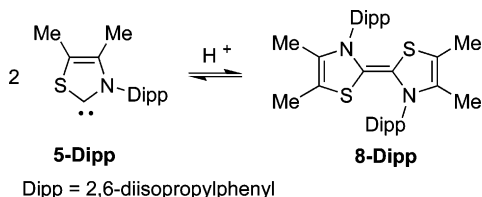
The role of steric effects of the substituents on the nitrogen atom was also evidenced for the isolation of the carbene. For instance, "smaller" groups such as 2,4,6-trimethylphenyl on the nitrogen proved to be insufficient to allow isolation of the corresponding carbene; it was only observed by NMR spectroscopy up to 0 °C in solution while with a methyl group only the dimer was observed (Scheme 10), isolated, and crystallographically characterized.

Scheme 10
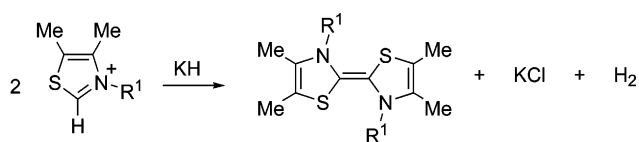
4-Mes R^1 = 2,4,6-mesityl   **8-Mes** R^1 = 2,4,6-mesityl
4-Me R^1 = methyl   **8-Me** R^1 = methyl

Figure 1 shows the molecular structures of DTDAFs **8**-Dipp and **8**-Me determined by X-ray crystallographic analysis.[30] In DTDAF **8**-Dipp, the two thiazole rings are planar with a twist of 5° about the central double bond. Bulky diisopropylphenyl substituents are located almost perpendicular to the thiazole rings. The structure of the hexamethyl-DTDAF **8**-Me is slightly different. As can be seen in Figure 1, distortions from planar geometry were observed.[30]
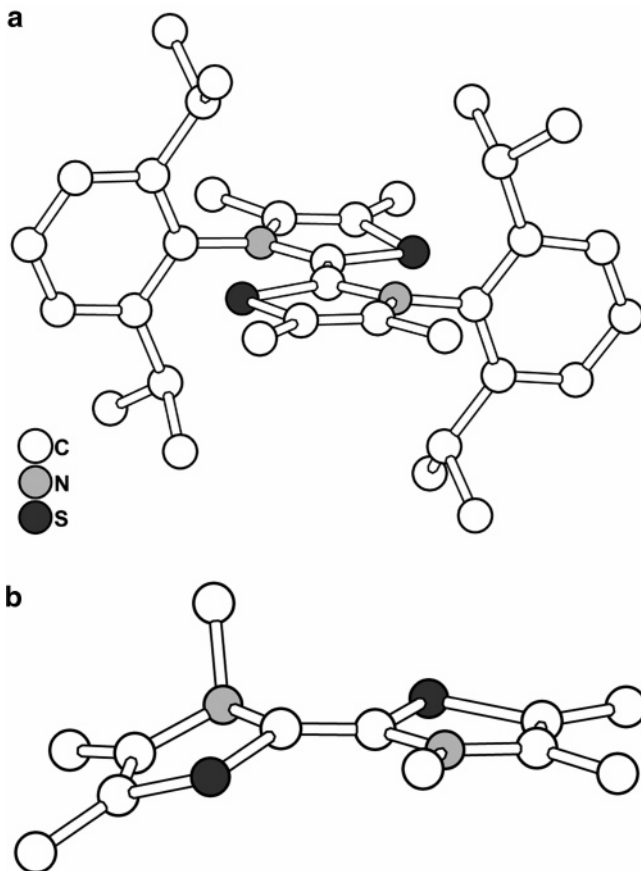
Figure 1. Molecular structures of DTDAF **8**-Dipp showing planarity of the donor core (top) and hexamethyl DTDAF **8**-Me showing distortion of the donor core (bottom).

2.2. Coupling of Thiazole Cores with Trivalent Phosphorus Derivatives (Route B)

Shortly after the first synthesis of DTDAF, Kleiner[47] reported a novel strategy to form DTDAF. He

Scheme 11

R^1 = CH$_3$, Ph   R = OEt, n-Bu, NMe$_2$
                3-Me R^1= Me
                3-Ph R^1= Ph
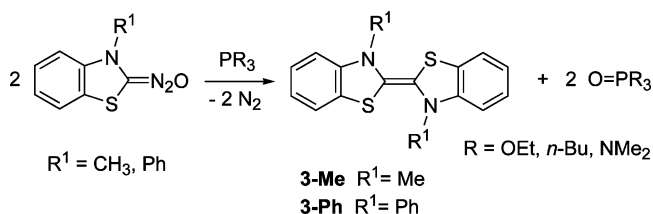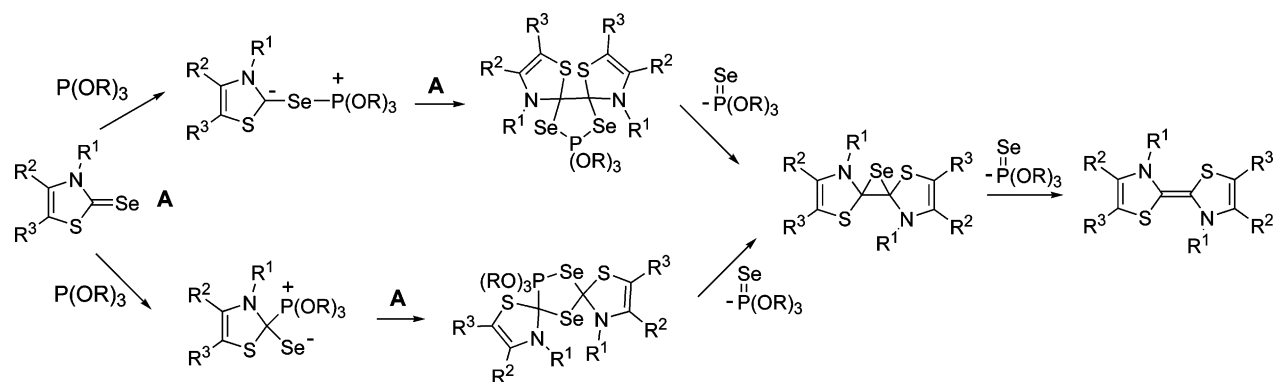
Scheme 12

demonstrated that in the absence of atmospheric oxygen, benzothiazoline-2-nitrosimino reacted with trialkyl phosphites, trialkylphosphines, or tris(dialkylamino)phosphines to form the fulvalene core in 63−77% yield (Scheme 11).

Cava et al. described another type of coupling in the presence of trivalent phosphorus derivatives in 1992.[48] They reported the synthesis of isolable DTDAFs from 1,3-thiazoline-2-selones in quantitative yield (Scheme 12). The stabilization of the donor was achieved by four electron-withdrawing substituents. This reaction was carried out by analogy with procedures employed in the dechalcogenization of 1,3-dithiole-2-selones, -2-thiones series for the synthesis of TTF.[4] The coupling of 1,3-thiazoline-2-selones A was performed in the presence of trialkyl phosphite. As postulated for the TTF series, a similar mechanism represented above can account for the formation of the donor core (Scheme 12). The different DTDAFs obtained via this route are listed in Tables 1−3.[42,47−55] It is worth noting that so far no coupling reaction of the thiazoline-2-thione, which is the starting material for the synthesis of the selones, in the presence of trivalent phosphorus derivatives, was observed as it was the case in the dithiole series for the synthesis of TTF.[4]

2.3. Electrochemical Synthesis (Route C)

Electrochemical reduction of 2-thioalkyl-1,3-thiazolium salts on a platinum electrode was shown to be an interesting pathway toward DTDAFs.[41,51−53,56] Even if no quantitative electrosynthesis has been described in the literature, this approach has allowed the formation of miscelleneaous DTDAFs and the determination of their redox properties, without isolation of the air sensitive derivatives. The formation of the donor occurs according to an ECE mechanism as outlined in Scheme 13. The first

Scheme 13
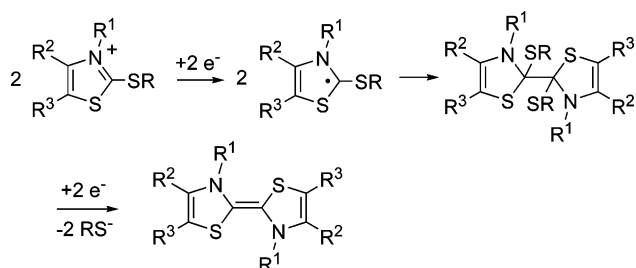
electrochemical step consists of the reduction of the thiazolium salt to its radical. The next step involves the coupling of two radicals to produce the tetrathio intermediate. The second electrochemical step corresponds to the reduction of this intermediate affording the desired DTDAF after the departure of two RS−. This synthesis is reminiscent of the preparation of TTF derivatives described by Moses and Chambers[57] where electrochemical reduction of 2-alkylthio-1,3-dithiolium salts afforded an ortho-thiooxalate intermediate. However, in this case, a thermolysis was needed to form the TTF derivative.

The formation of the donor core can be followed by cyclic voltammetry as can be seen in Figure 2. On the first cathodic scan, an intense reduction peak is observed while on the reverse scan, two oxidation peaks are observed corresponding to the signature of the DTDAF formed in the medium during the reduction (vide infra).
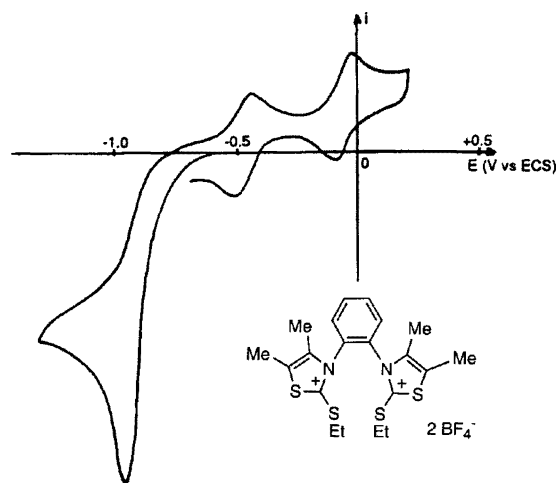
Figure 2. Cyclic voltammogram of the represented N,N'-bridged bis-thiazolium salt, 1 M Bu$_4$NPF$_6$, CH$_3$CN, Pt electrode, and 0.1 V s^{-1} vs SCE.

2.4. Alkylation of 2,2′-Bithiazole (Route D)

Hünig et al.[58] studied the formation of DTDAF starting from 2,2′-bibenzothiazole. The alkylation of **9** with strong alkylating agents such as trimethyl oxonium tetrafluoroborate allowed the preparation of the DTDAF dication **3**-Me^{2+}, which can be further reduced into DTDAF **3**-Me (Scheme 14). Dimethyl

Scheme 14
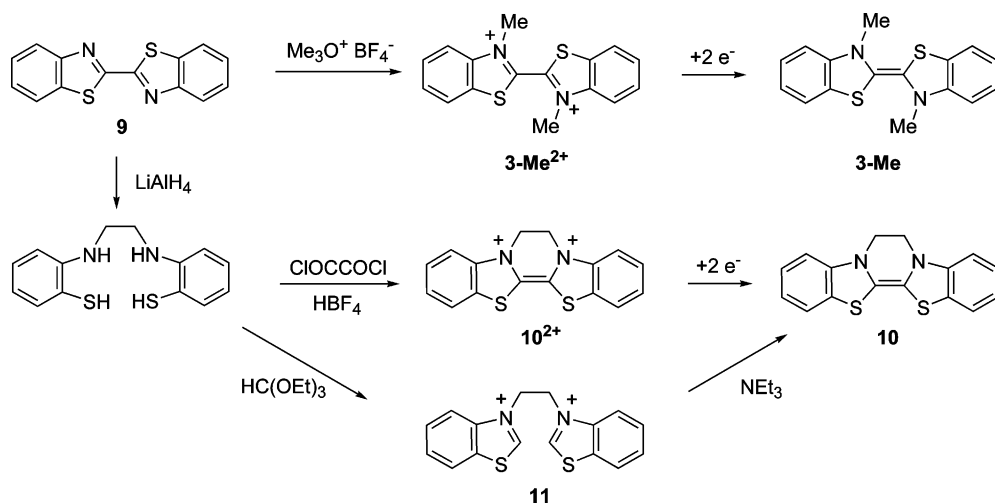
sulfate was also used as an alkylating agent of 2,2′-bithiazole **9**.[59,60] Interestingly, the reduction of **9** by LiAlH$_4$ afforded the 1,2-bis(o-mercaptoanilino)ethane, which reacts either with oxalyl chloride to give the dicationic intermediate **10**$^{2+}$ or with ethyl orthoformate to give the *N,N′*-ethylene bis benzothiazolium salt **11**, both precursors of *N,N*-ethylene-bridged bisbenzo-DTDAF (Scheme 14).[58]

The synthesis of 2,2′-bithiazolium salts from 2,2′-bithiazole was also examined by Thummel and co-workers.[61] They noticed that 2,2′-bithiazole treated with methyl iodide gives only the monomethylated derivative while the reaction of 2,2′-bithiazole with α,ω-dihaloalkanes affords the cor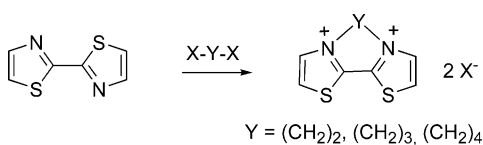responding *N,N′*-alkylene-bridged 2,2′-bithiazolium salts (Scheme 15). The reduction of these salts was realized electrochemically (vide infra).

Scheme 15

Miscellaneous method: In their study of the reactivity of thiazol-2-stannanes, Jutzi and Gilge[62] mentioned the formation of DTDAF in moderate yields by reaction with acetyl chloride or chloromethylmethyl ether (Scheme 16).

Scheme 16

3-COMe R^1 = COMe, 19%
3-CH$_2$OMe R^1 = CH$_2$OMe, 39%
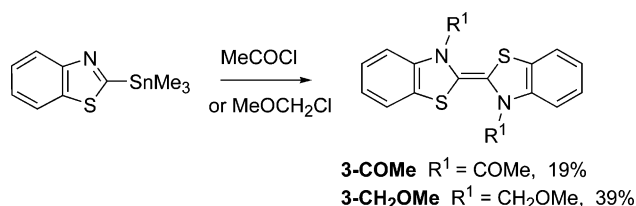
The postulated mechanism for the formation of DTDAF is presented in Scheme 17 below. The adduct A of acetyl chloride to the thiazole ring, after the loss

of Me$_3$SnCl, leads to the ylide B, which reacts with the adduct A to form DTDAF **3**-COMe.

Scheme 17
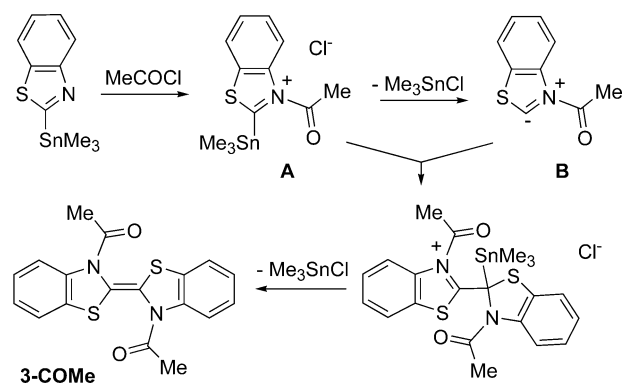
3. Chemical Oxidations and Rearrangements

3.1. Oxidations

As mentioned by Vorsanger,[9] all of the investigations carried out on DTDAFs were faced with one difficulty: the instability of the dimer upon air exposure. For instance, it was shown that *N,N′*-dimethyl benzo-DTDAF **3**-Me led upon air exposure to various structures of oxygen-containing products, mainly the cyclodecane **12** but also the ketospiran **13** and decomposition products such as the spiran **14** (Scheme 18).[9,25,26]

Scheme 18
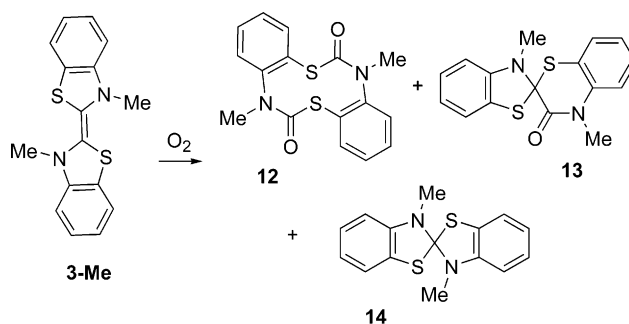
This gave the first evidence that this family of π-donor molecules was oxygen sensitive. It is worth noting that the spiro amide derivative **13** was obtained in quantitative yield by mixing **3**-Me with sulfur dioxide.[63] In this case, the reaction followed by electron spin resonance (ESR) experiments proceeds through the cation radical intermediate. Similarly, oxidation of **3**-Me with AgBF$_4$ led to the formation of the dication **3**-Me^{2+} together with the spiroamide derivative **13** (Scheme 19).[55]

Scheme 19
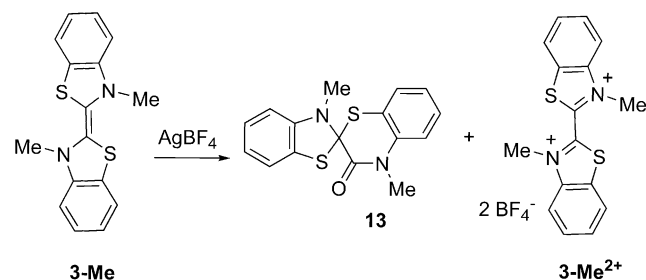
Furthermore, Baldwin and Walkers, while leaving a CH$_2$Cl$_2$ solution of **3**-Me upon oxygen exposure at 0 °C, found out that the cyclodithiadiazecinedione **15**-Me, originally formulated as the isomeric cyclic thiocarbamate **12**, was obtained in high yield.[64]

Murphy et al. realized the synthesis of **3**-Et and its purification without exclusion of air and obtained the cyclodithiadiazecinedione **15**-Et as the major compound.[40] The proposed mechanism involves first the reaction of **3**-Et with dioxygen to form 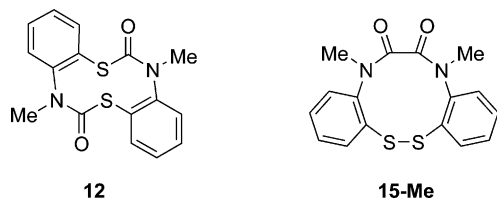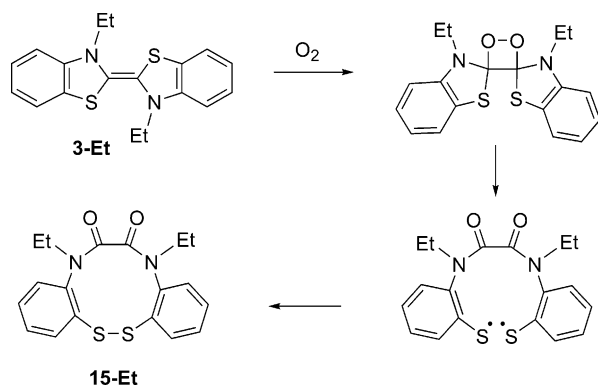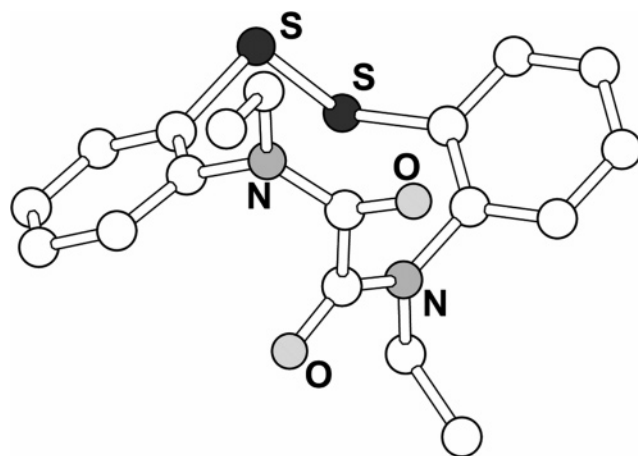the superoxide radical anion and then the intermediate dioxetane, followed by the cleavage of the O–O bond to form a diradical and fragmentation to the bis-thiyl radical and formation of the macrocycle (Scheme 20). The molecular structure of **15**-Et was

Scheme 20

established by X-ray crystallography confirming the findings of Baldwin et al. on the evolution of benzo-

Figure 3. Molecular structure of the cyclodiazecinedione **15**-Et.

DTDAF **3** upon air exposure (Figure 3). Similar cyclodithiadiazecidiones were also obtained with non-benzoannelated-DTDAF.[39]

One could suppose that the air oxidation of the DTDAF was correlated with the redox potentials of the donor (see Electrochemical Behavior), but as noticed by Cava et al., even DTDAF substituted by four electron-withdrawing groups led also to oxidation products by recrystallization in the presence of air.[49] Therefore, all DTDAFs seem labile to oxygen and oxidative rearrangements would occur more or less rapidly depending on the substituents on the donor core.

Other means, such as the reaction of 3,3′-dimethyl-2,2′-bithiazolium salts with potassium superoxide, lead to the same ten-membered ring compounds, which were crystallographically characterized (Scheme 21 and Figure 4).[59,60,65]

Scheme 21
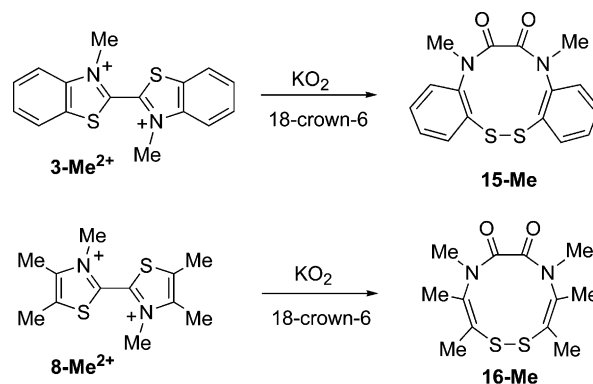
Controlled oxidation, to the DTDAF dication, was performed in order to avoid any undesired oxidation products. Investigations carried out on these salts are somehow easier as they can be handled and recrystallized under atmospheric conditions without any particular precautions. The dication can be prepared either according to the above procedure, e.g., alkylation of 2,2′-bithiazole derivatives (route D, Scheme 4),[58–61] or by adding an oxidizing agent in the medium where the neutral donor was formed under an inert atmosphere.

a

b
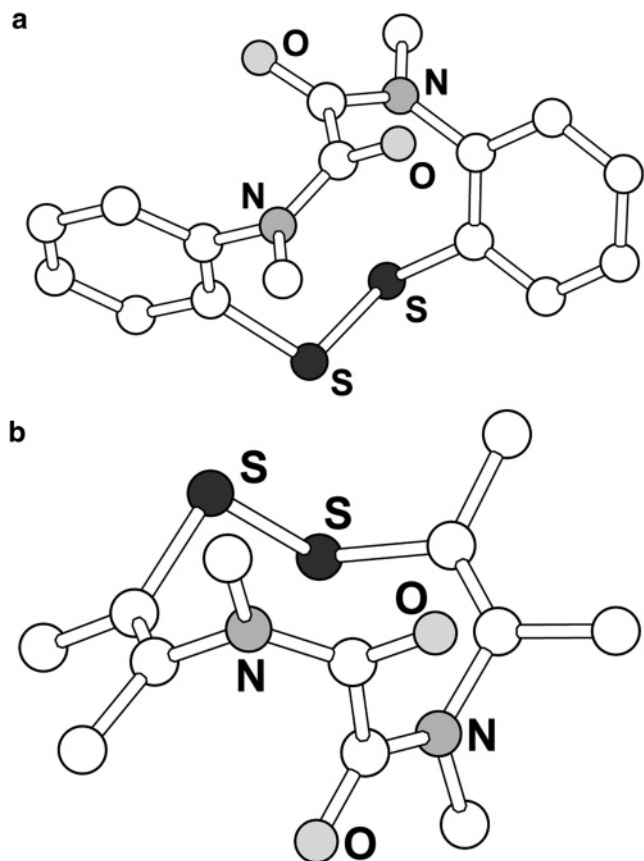
Figure 4. Molecular structures of **15**-Me (top) and **16**-Me (bottom).

Several chemical oxidizers have been used to generate the dication salts of DTDAF. They were first mentioned by Metzger et al. in 1964 in his study of the reactivity of DTDAF.[10] Bis benzannelated DTDAFs were oxidized with solutions of bromine, iodine, or silver ion to afford the dication salts as yellow to red solids depending on the counterions (Scheme 22).[55,58]

Scheme 22
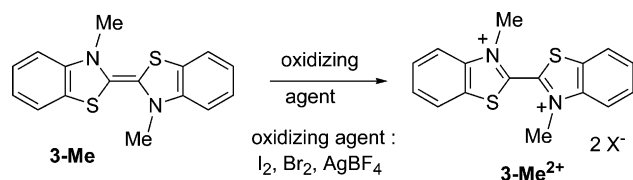
Recrystallization of (**3**-Me^{2+})(BF$_4^-$)$_2$ from the HCOOH/MeCOOH mixture afforded the dication as pale yellow crystals suitable for X-ray diffraction. The molecular structure of this dication is represented in Figure 5. An interesting feature concerns the geometry of this dication; both heterocyclic cores are
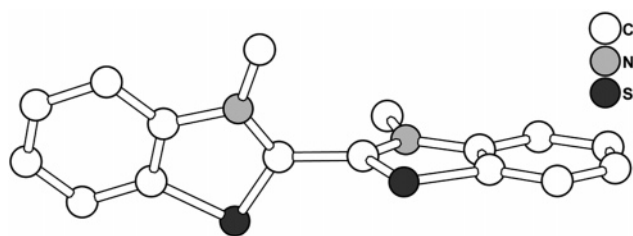
Figure 5. Molecular structure of **3**-Me^{2+} as a BF$_4^-$ salt.

planar but located in planes almost perpendicular to each other.[55] This nonplanar geometry for the dication species obtained from N,N'-dimethyl DTDAF is another particularity belonging to the DTDAF family (vide infra).

Tormos et al. used phenyliodoso diacetate in the presence of perchloric acid in dioxane to oxidize electron-withdrawing substituted DTDAF.[48–50] Other agents were used, such as NOBF$_4$ and HBF$_4$, to oxidize the N,N'-phenylene-bridged DTDAF **17** into the dication **17**$^{2+}$ (Scheme 23).[53] The later reagent was also used for the generation of radical cation salts in the TTF family.[66]

Scheme 23
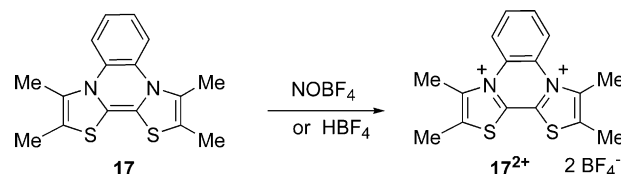
3.2. Rearrangements

Rearrangements of N-allyl and N-benzyl-DTDAF have also been observed.[25,35,37,38,64] A first structure was proposed by Wanzlick who suggested that the dimer **18** was formed due to the reaction of the tautomeric form of the ylide (Scheme 24).[25] Furthermore, Baldwin and co-workers reinvestigated the dimer rearrangement and found out that the structure **18** was incorrectly formulated and that **19** was formed instead. They also elucidated the mechanistic details and demonstrated that these dimers **3**, preliminary formed in the medium, undergo a 1,3-sigmatropic rearrangement (Scheme 24).[35] Similar results were also obtained from dimers that stem from thiamin.[37]

Scheme 24
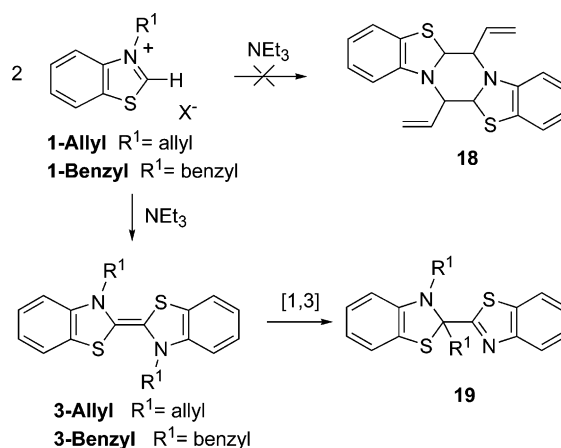
4. Electrochemical Behavior

DTDAFs present similar redox behaviors to their well-known sulfur analogues, the TTFs. They exhibit three oxidation states: neutral, cation radical, and dication where the two electrons are transferred in a stepwise fashion (Scheme 25). These two families of π-donor molecules, DTDAF and TTF, belong to the

Table 4. Oxidation Potentials of DTDAF According to Substituents

Donors	R^1	R^2	R^3	$E_1{}^a$	$E_2{}^a$	ΔE^b	••••••	Ref.
				-0.17	-0.02	150	CH_3CN^c	69
				-0.18	-0.08	100	CH_2Cl_2	55
	Me	H	H	-0.54	-0.41	130	DMSO	61
	Me	Me	COMe	-0.31	-0.06	250	CH_3CN	52
	Me	Me	CO_2Et	-0.33	-0.11	220	CH_3CN	52,54
	Me	CO_2Me	CO_2Me	-0.02	+0.23	250	CH_3CN	49
	Me	CN	CN	+0.38	+0.59	210	CH_3CN	49
	Ph	SMe	CO_2Me	-0.06	+0.43	490	CH_3CN	48,49
	Ph	CO_2Me	CO_2Me	+0.09	+0.57	480	CH_3CN	49
	Ph	Me	COMe	-0.23	+0.21	440	CH_3CN	53
	Ph	Me	$CMe=C(CN)_2$	-0.13	+0.19	320	CH_3CN	53
	Ph	SMe	$p\text{-}ClC_6H_4$	-0.27	+0.05	320	CH_3CN	75
	$p\text{-}NO_2C_6H_4$	SMe	$p\text{-}ClC_6H_4$	-0.07	+0.12	190	CH_3CN	39
	CH_2CO_2Et	Me	CO_2Et	-0.11	+0.36	470	CH_3CN	54

^{a} Oxidation potentials are given in volts vs SCE, Pt electrode, supporting electrolyte Bu_4NPF_6. ^{b} ΔE is given in mV. ^{c} E_1 and E_2 were determined by polarography and are vs Ag/AgCl.

Weitz type where the heteroatoms are members of the cyclic π-systems showing "quinoid" structure in the neutral form while in the oxydized form, e.g., the dicationic state, they exhibit "aromatic" behavior.[67]
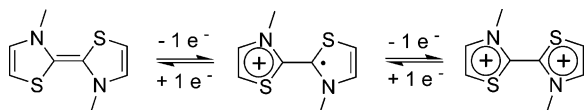
Scheme 25

The 3,3′-dimethyl dibenzo DTDAF **3**-Me was the first of this family of π-donor molecules that was characterized electrochemically starting from either the neutral or the dication form.[67–70,55] These investigations were carried out either by polarography or by cyclic voltammetry. On the voltammograms, this derivative exhibits two reversible monoelectronic waves. No significant difference was observed on the redox values using the neutral or the oxidized form, and for **3**-Me^{2+}, two close redox steps were observed at $E_1 = -0.17$ V and $E_2 = -0.02$ V vs Ag/AgCl.[68] The oxidation potentials are at very low potentials, making **3**-Me extremely labile to oxygen upon air exposure (see above). As noticed by Hünig, this derivative is better isolated under the oxidized dicationic form than in its neutral form.[69] Interestingly, if we compare these potentials with those of the corresponding member of the TTF family, the dibenzo-TTF[71] ($E_1 = 0.72$ V and $E_2 = 1.06$ V vs Ag/AgCl),[72] one can observe a potential difference of about 900 mV for the first oxidation step, indicating excellent electron-donating properties of the DTDAF core. Moreover, the presence of a N-Me instead of a sulfur atom has the effect of decreasing the difference between the two oxidation potentials ($\Delta E = E_2 - E_1 = 340$ mV for dibenzo-TTF and 150 mV for **3**-Me) and therefore lowering the thermodynamic stability of the cation radical species ($K = 5.6 \times 10^5$ for TTF while for DTDAF $K = $

3.5×10^2, with $K = [D^{+\bullet}]^2/[D][D^{2+}]$). This decrease was first attributed by Hünig et al. to disturbed coplanarity. Indeed, when they studied the electronic absorption spectra realized on the dication, an absorption maximum at about 280 nm was observed. Actually, the structure of the dication depicted in Figure 5 unambiguously confirmed the Hünig hypothesis about the disturbed coplanarity.[55]

Further electrochemical investigations were devoted to nonbenzo-fused DTDAF derivatives. Indeed, benzofusion hampers modulation of the redox properties while substitution on the 4,4′ and 5,5′ positions with various electron-donating groups or electron-withdrawing groups leads to donor cores exhibiting a vast range of redox potentials (-0.54 V $< E_1 < 0.38$ V vs SCE); see Table 4. The only positive values (vs SCE) were observed for the DTDAFs substituted by four electron-withdrawing substituents; consequently, these compounds are the only isolated nonbenzo-fused DTDAFs. Concerning the other DTDAFs, the redox potentials were determined by cyclic voltammetry directly in the medium where the donor was formed, under an inert atmosphere, to avoid the formation of nondesired oxidation products. For most of the N-methyl derivatives, a small ΔE can be observed. The hexamethyl DTDAF **8**-Me was not characterized by cyclic voltammetry, but one can assume a similar redox behavior. This donor is of interest as it was the only representative that was characterized by X-ray crystallography under its neutral form[30] and also as a dication.[52] The dicationic salt of the hexamethyl-DTDAF **8**-Me^{2+} is not planar (Figure 6); the two thiazole rings are twisted around the central C−C bond by an angle of 76.6°. Upon oxidation, DTDAF (**8**-Me), almost planar in the neutral state (Figure 1),[30] undergoes upon oxidation a rotation of the two thiazole rings around the central C−C bond (see Scheme 26).[52] Similar twists are
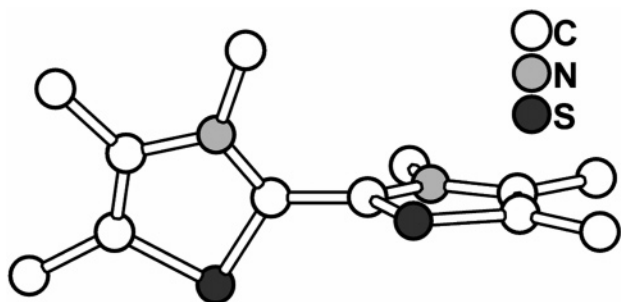
Figure 6. Molecular structure of the hexamethyl DTDAF dication **8**-Me^{2+} in the TCNQ complex (DTDAF **8**-Me)-(TCNQ)$_3$.

observed in dicationic TTF^{2+} salts;[73] albeit planar TTF dications have been also reported.[74] This suggests that DTDAFs have a stronger tendency to twist upon oxidation than the TTF analogues.

Scheme 26
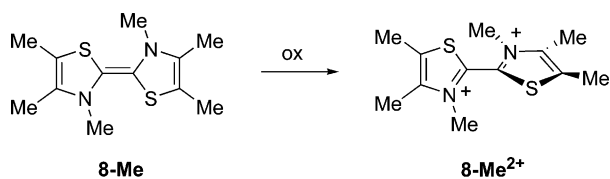
Another interesting feature is the ΔE ($E_2 - E_1$) increase observed for the N-phenyl-substituted derivatives when compared to the N-methyl one. As suggested by Cava et al., the presence of the aromatic group induces a greater charge delocalization and gives added stability to the cation radical species.[49] Indeed, Robert and co-workers have solved the structure in a 1:5 complex of the N-phenyl-substituted DTDAF **20**-Ph with TCNQ (vide infra), and the oxidized DTDAF core exhibited a planar structure with the phenyl substituents located in perpendicular planes to the one formed by the donor core (Figure 7).[75]

Figure 7. Molecular structure of DTDAF **20**-Ph (R^1 = Ph, R^2 = SMe, R^3 = p-ClC$_6$H$_4$) in the TCNQ complex (DTDAF **20**-Ph)(TCNQ)$_5$.
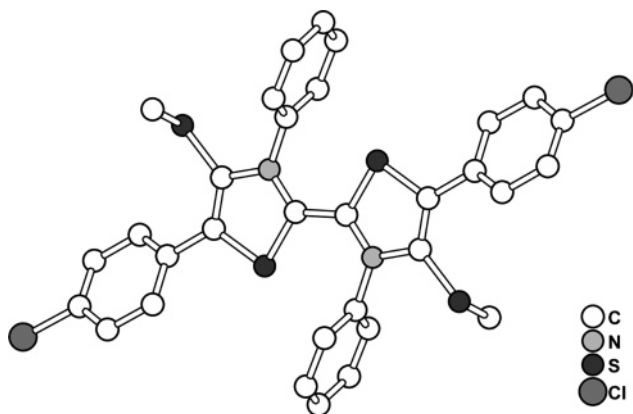
N,N'-Bridged DTDAF such as N,N'-phenylene- or N,N'-ethylene-bridged DTDAF were also investigated by cyclic voltammetry. Hünig studied the N,N'-ethylene-bridged dibenzoDTDAF **10**, and he observed that by restoring planarity, as compared with N,N'-dimethyl derivatives, the ΔE reached a value of 490

mV ($K = 2 \times 10^8$).[69] Analysis of the electronic absorption spectra of the dication showed an absorption maxima at about 400 nm. In this series, all of the donors exhibit two well-separated reversible monoelectronic oxidation waves with the first oxidation potential varying with the substituents from -0.72 to -0.10 V vs SCE (see Table 5). Depending on the substituents, DTDAF shows now a potential difference between the second and the first oxidation potential larger than a value of 410 mV. In this case, the presence of the short bridge hinders any conformational modification upon oxidation such as the ones previously observed for the N-methyl derivatives. Therefore, the values of ΔE are the results of increased electronic interactions in the oxidized species. The structure of the N,N'-phenylene-bridged DTDAF **17** cation radical species shown in Figure 8 demonstrates the rigidification brought to the donor core by the N,N'-bridge.[51]
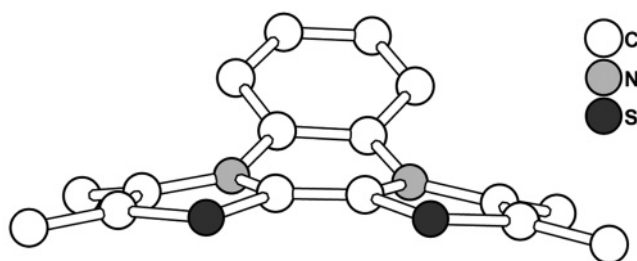
Figure 8. Molecular structure of N,N'-phenylene-bridged DTDAF **17** radical cation in the complex (DTDAF **17**)$_2$-(Mo$_6$O$_{19}$).

Other bridged systems were investigated electrochemically. Thummel et al. noticed the effect of the N,N'-bridge length—from two to four carbons—by studying the reduction of bisthiazolium salts.[61]

n = 2-4
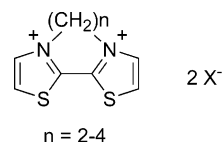
They found that ΔE decreases when the length increases until reaching only one single nearly irreversible wave for the N,N'-butylene-bridged DTDAF. Electronic absorption spectra performed on starting bisthiazolium salts demonstrated that when the length of the N,N'-bridge increases from two to four carbons, the absorption maxima decreases from 346 to 295 nm close to the 270 nm found for the corresponding N,N'-dimethyl DTDAF. This high energy absorption was attributed to a large dihedral angle between the thiazolium rings. Actually, the bridging chain is probably long enough to allow the molecular movements observed previously for the nonbridged systems, upon oxidation.
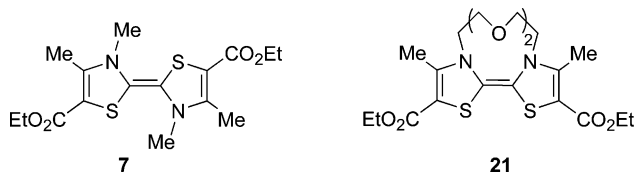
Table 5. Oxidation Potentials of DTDAF According to Substituents

Donors	n	R^2	$R^{2'}$	R^3	$R^{3'}$	$E_1{}^a$	$E_2{}^a$	ΔE^b	solvent	Ref.
						-0.23	+0.26	490	CH_3CN^c	69
						-0.24	+0.30	540	CH_2Cl_2	55
	2	H		H		-0.68	-0.13	550	CH_3CN	41
	2	Me		H		-0.69	-0.15	540	CH_3CN	41
	2	Me		Me		-0.72	-0.25	470	CH_3CN	41
	2	Me		CO_2Et		-0.30	+0.25	550	CH_3CN	41
	2	Me		COMe		-0.27	+0.16	430	CH_3CN	41
	2	H		H		-0.57	-0.13	440	DMSO	61
	3	H		H		-0.50	-0.13	370	DMSO	61
	4	H		H			-0.42^d		DMSO	61
		Me	Me	Me	H	-0.54	-0.05	490	CH_3CN	56
		Me	Me	Me	Me	-0.47	-0.06	410	CH_3CN	51
		Me	Me	Me	CO_2Et	-0.33	+0.09	420	CH_3CN	56
		Me	Me	CO_2Et	CO_2Et	-0.10	+0.41	510	CH_3CN	56
		H		H		-0.54	-0.36	180	CH_3CN	42
		Me		H		-0.56	-0.37	190	CH_3CN	42
		Me		Me		-0.62	-0.51	110	CH_3CN	42
		Me		CO_2Et		-0.24	-0.01	230	CH_3CN	42
		Me		COMe		-0.22	-0.03	190	CH_3CN	42

[a] Oxidation potentials are given in volts vs SCE, Pt electrode, supporting electrolyte Bu_4NPF_6. [b] ΔE is given in mV. [c] E_1 and E_2 were determined by polarography and are vs Ag/AgCl. [d] One nearly irreversible wave ($\Delta E_p = E_{pa} - E_{pc} = 320$ mV).

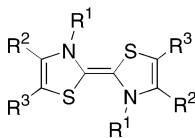Crown ether annelated DTDAFs were also investigated.[42] Interestingly, the comparison of the redox potentials of **21** with the N,N'-dimethyl DTDAF **7**, bearing the same exocyclic substituents R^2 and R^3, displays a close redox behavior and a similar ΔE in both cases ($\Delta E = E_{pa2} - E_{pa1} = 190$ mV) indicating that the N,N'-bis oxa ethyl chain is long enough for allowing similar modifications. The complexation of various alkali metal ions (Li^+, Na^+, K^+) on this crown-ether annelated DTDAF was studied by electrochemistry. The metal binding effect was only observed for the smallest one and ascribed to the correlation between the hole size of the cavity and the radius of Li^+. An anodic shift, due to electrostatic repulsion with the bound metal cation, was observed for both oxidation processes (15 mV for the first one and 45 mV for the second) indicating that the metal was complexed with the crown annelated DTDAF **21** during the two processes. Contrariwise, no effect was detected on the reduction waves indicating that the metal ion was expelled from the cavity only after the second oxidation process. This behavior is markedly different from what was observed with crown-ether annelated TTF in the presence of alkali metal ions where the first oxidation is usually shifted anodically whereas the second oxidation remained unchanged indicating that the metal ion is expelled upon oxidation to the cation radical.[76] Therefore, the presence of the metal could account for the stabilization of the cation radical species by complexing the side chain and maintaining the thiazole cores in the same plane.

5. DTDAF as Precursors of Molecular Materials

5.1. Charge Transfer Salts

The very first charge transfer complexes based on DTDAF were described by Wheland in 1976.[24] They were prepared from the relatively stable benzannelated-DTDAF **3**-Me by simply mixing the donor with organic acceptors such as TCNQ, dimethoxy-TCNQ [TCNQ(OMe)$_2$], or bis(2-butene-2,3-dithiol) platinum complex [Pt($C_2S_2Me_2$)$_2$] in acetonitrile. Other acceptors were investigated as well with various DTDAFs, including the bis-1,2,5-thiadiazolotetracyanoquinodimethane (BTDA-TCNQ),[77] C_{60},[78-80] I_2,[78] TCNQF$_4$,[78] and ($Mo_6O_{19}{}^{2-}$)[51] (Table 6). In most cases, the simple mixing of DTDAF and acceptor moieties only afforded powders that were characterized by (i) elemental analysis (to determine the donor:acceptor ratio), (ii) IR spectroscopy (to determine the ν_{CN} vibration and hence the degree of charge transfer on the TCNQ moieties), and (iii) conductivity measurements on compressed pellets. Note that for anisotropic materials, conductivity measurements on compressed pellets are usually considerably lower than on single crystals due to no selective orientation that may occur during the formation of the pellet. For instance, compaction conductivity measurements on TTF-TCNQ are considerably lower (10 S cm^{-1}) than on single crystals along the long axis (417 S cm^{-1} at room temperature).[24] Therefore, the very first values of conductivity observed on the complexes involving

Table 6. Charge Transfer Complexes of DTDAF with Various Acceptors

	R^1	R^2	R^3	acceptors	$E_1{}^a$	conductivity^b	D:A ratio	ref
		donors/redox potentials						
3-Me	Me		$-CH=CH-CH=CH-$	TCNQ	0.17	5×10^{-2}	1:3	24
	$E_1 = -0.17$ V; $E_2 = -0.02$ V			TCNQ(OMe)$_2$	-0.01	3.3×10^{-2}	1:2	24
				Pt(C$_2$S$_2$Me$_2$)$_2$	0.98	5×10^{-7}	1:1	24
				BTDA-TCNQ	-0.02	2×10^{-2}	1:3:1H$_2$O	77
22-Ph	Ph	SMe	CO$_2$Me	TCNQ	0.17	1.6×10^{-7}	1:1	49, 50
	$E_1 = -0.06$ V; $E_2 = 0.43$ V			TCNQ	0.17	1.1×10^{-7}	1:4:2CH$_3$CN	49, 50
				C$_{60}$			1:2:1CS$_2$	80
23-Me	Me	CO$_2$Me	CO$_2$Me	TCNQ	0.17	8.3×10^{-2}	1:4	49, 50
	$E_1 = -0.02$ V; $E_2 = 0.23$ V							
23-Ph	Ph	CO$_2$Me	CO$_2$Me	TCNQ	0.17	$<10^{-10}$	1:1	49, 50
	$E_1 = 0.09$ V; $E_2 = 0.57$ V			TCNQ	0.17	1.1×10^{-2}	2:5	49, 50
				TCNQF$_4$	0.53	1.2×10^{-6}		78
				C$_{60}$		$<10^{-10}$		78
				I$_2$		1.1×10^{-7}		78
				I$_2$		$<10^{-10}$		78
20-Ph	Ph	SMe	p-ClC$_6$H$_4$	TCNQ	0.17	$6 \times 10^{-4\,c}$	1:5	39
	$E_1 = -0.27$ V; $E_2 = -0.05$ V							
8-Me	Me	Me	Me	TCNQ	0.17	$1.25 \times 10^{-2\,c}$	1:3	52
17	o-C$_6$H$_4$	Me	Me	TBA$_2$(Mo$_6$O$_{19}$)	-0.32		2:1	51
	$E_1 = -0.47$ V; $E_2 = -0.06$ V							

^{a} First reduction potential of the acceptor in volts. ^{b} Conductivity in S/cm for two-probe method, room temperature, compaction. ^{c} Four-probe method on single crystal.

DTDAF (10^{-2} S cm^{-1}) were encouraging. In most examples, however, in the absence of crystal structure, we are limited to conjectures for the evaluation of the degree of charge transfer, essentially based on the stoichiometry of the salts, their conductivity, and the relative redox potentials of the DTDAF and of the acceptor.

For example, considering the first described 1:3 salt of DTDAF with TCNQ, (**3**-Me)(TCNQ)$_3$, the comparison of redox potentials (Table 6) indicates that the donor molecule is most probably oxidized to the dicationic diamagnetic state; hence, the three TCNQs have a whole dianionic charge. This mixed valence state of the radical anions can explain the relatively high conductivity of the salt, which is most probably attributable to the TCNQ stacks. The reduction potential of the weaker TCNQ(OMe)$_2$ oxidizer closely matches the second oxidation potential of DTDAF **3**-Me. The oxidation state of the DTDAF in the 1:2 salt with TCNQ(OMe)$_2$, (**3**-Me)(TCNQ(OMe)$_2$)$_2$, is therefore difficult to estimate (1+ or 2+). In the first case, the two TCNQ(OMe)$_2$ would exhibit a mixed valence state and a sizable conductivity while in the second case, the two TCNQ(OMe)$_2$ would be reduced to the radical anion state and the salt should be insulating. The 3.3×10^{-2} S cm^{-1} conductivity for this salt favors the first situation, that is, (**3**-Me$^{+\bullet}$)-[TCNQ(OMe)$_2$]$_2{}^{-\bullet}$, and indicates that efforts should be pursued for isolating this salt in a crystalline form.

Starting from isolable DTDAFs where the stabilization was achieved through the presence of electron-withdrawing groups, Cava and collaborators isolated five new charge transfer complexes with TCNQ,[49,50] which could not be crystallographically characterized. Considering the redox potential of these donor mol-

ecules, the N-Ph DTDAFs **22**-Ph and **23**-Ph are expected to be oxidized to the cation radical state while the situation of the N-Me DTDAF **23**-Me is unclear given the close proximity of its second oxidation potential (0.23 V) with the reduction potential of TCNQ (+0.17 V). Indeed, the 1:1 salts of the N-Ph DTDAF (**22**-Ph)(TCNQ) and (**23**-Ph)(TCNQ) are insulating ($\sigma = 10^{-7}-10^{-10}$ S cm^{-1}), a probable consequence of (i) the full charge transfer on the TCNQ moieties, which will favor their association into diamagnetic dimers or into weakly interacting stacks (Mott insulator), and (ii) the presence of the bulky phenyl rings, which most probably hinder, as already observed by Robert and co-workers,[75] any $\pi-\pi$ stacking of the donor, even in their radical cation state. Considering now the 2:5 TCNQ salt (**23**-Ph)$_2$(TCNQ)$_5$, EPR investigations carried out on a solution obtained by dissolving the complex allowed the observation of the signals due to the presence of both the cation radical and the anion radical species,[49] thus confirming the above analysis of the redox potentials. Contrariwise, similar experiments on a solution of **23**-Me and TCNQ exhibited only the anion radical signal,[49] presumably due to the fact that the donor was oxidized to the dication, as anticipated from the close proximity of the redox potentials (see above).

Let us now analyze those TCNQ salts, the crystalline structure of which has been described in detail. In 1993, Robert et al. reported the in situ generation of a charge transfer complex involving DTDAF **20**-Ph with TCNQ.[39] The synthetic strategy used to form the air sensitive **20**-Ph (R^1 = C$_6$H$_5$, R^2 = SMe, and R^3 = p-ClC$_6$H$_4$) allowed the addition of TCNQ in the medium during the synthesis without purification of the donor. The nitrile stretching absorption band of
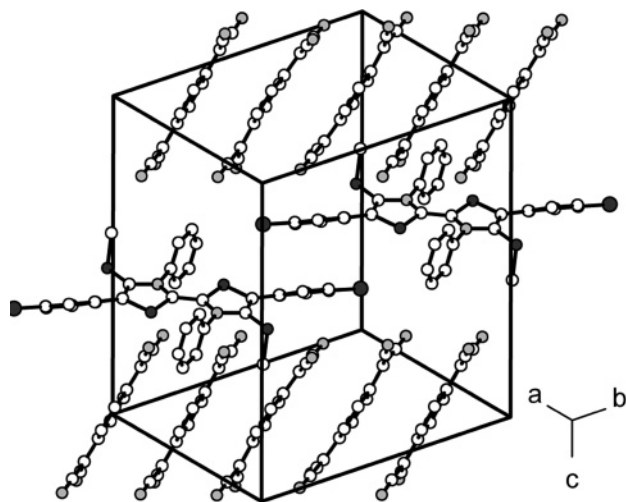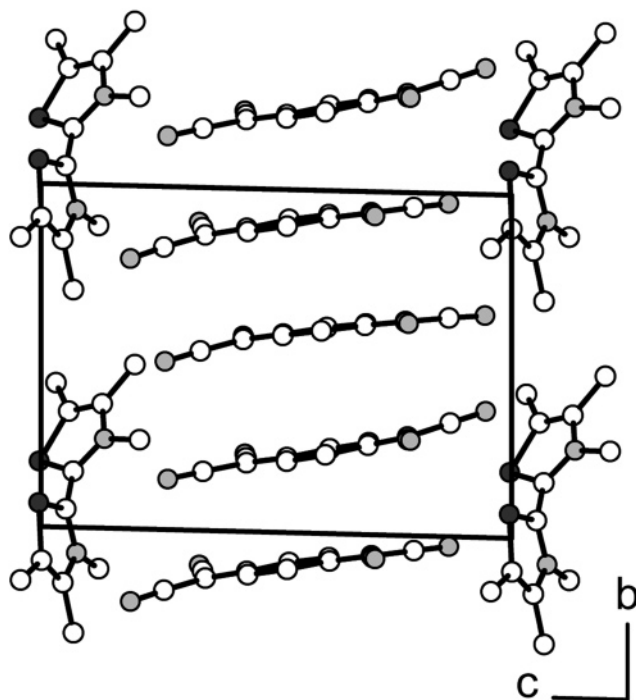
Figure 9. View of the molecular packing of (DTDAF **20**-Ph)(TCNQ)$_5$.

the complex in the FTIR spectrum (2194 cm^{-1}) shows a shift from the ν_{CN} value of neutral TCNQ (2227 cm^{-1}), suggesting a partial charge transfer from DTDAF to TCNQ.[81] The first X-ray crystal structure for this family of donors gave a valuable insight into the organization of the donor and the acceptor and the determination of the stoichiometry (1 DTDAF:5 TCNQ).[75]

The TCNQ forms segregated stacks with three crystallographic distinct TCNQ molecules (A, B, and C), arranged according to the sequence ···ABCBA··· It was not possible to evaluate the degree of charge transfer on TCNQs by using the empirical formula of Kistenmacher,[82] which correlates the bond lengths to the formal charge of TCNQ, because of the low quality of the crystal data. However, comparison of the central C−C bond length [1.48(1) Å] of the donor with the central C−C bond length observed in the neutral hexamethyl DTDAF [1.341(2) Å][30] or in its dication salt [1.469(4) Å][52] favors a dicationic state for the donor in this (DTDAF **20**-Ph)(TCNQ)$_5$ complex, in accordance with the redox potentials of the donor ($E_1 = -0.27$ V and $E_2 = 0.05$ V vs SCE) and the TCNQ (0.17 V vs SCE). Thus, the dications located between the stacks of TCNQ play a role of counterion (Figure 9). The room temperature single crystal four-probe conductivity of 6×10^{-4} S cm^{-1} is consistent with electron delocalization along the mixed valence TCNQ stacks.

Taking into account the steric effect brought by the N-phenyl group in (**20**-Ph)(TCNQ)$_5$, Lorcy et al. prepared the less hindered hexamethyl-DTDAF **8**-Me and trapped it in situ with a solution of TCNQ.[52] Black shiny crystals were isolated, and their crystal structure determination revealed a stoichiometry of one donor for three TCNQ. The analysis of the packing showed that the stacks of TCNQ molecules are separated from each other by the nonplanar donor molecules (Figure 10). Three TCNQs are crystallographically independent with different overlaps and a nonuniform intermolecular spacing within the trimeric entities, 3.486(76) and 3.216(27) Å, respectively. Between the pseudo trimers, a shorter interplanar separation is observed with a longitudinal slip

Figure 10. View of the molecular packing of (DTDAF **8**-Me)(TCNQ)$_3$ projected in the bc plane showing the TCNQ stacks sandwiched by the DTDAF dication.

[3.126(27) Å]. As mentioned above, the two thiazole rings of the donor are twisted around the central C−C bond by an angle of 76.6° preventing any stacking of the donors. EPR studies carried out on a single crystal showed only the presence of TCNQ radical anion; no signal was observed for the donor. FTIR spectra of the complex exhibited a broad nitrile stretching absorption band at 2197 cm^{-1} confirming the presence of reduced TCNQ moieties in the complex. All of these observations together with the empirical calculation of the formal charge on the three TCNQs, based on the bond length variation,[82] and the relative redox potentials of DTDAF **8**-Me and TCNQ, are in agreement with a dicationic state of the donor. Electrical conductivity measured on a single crystal using a four-point method amounts to 1.25×10^{-2} S cm^{-1} along the stacking direction and 1.3×10^{-3} S cm^{-1} along the perpendicular c-axis. The temperature dependence of conductivity suggests that electrical transport along the long axis of the crystal can be described by the variable range hopping model, while in the perpendicular direction the model of band semiconductor with constant energy gap $\Delta E = 0.29$ eV can be applied. Thus, only the TCNQs are participating in the π-electron conduction while the diamagnetic DTDAF^{2+} works as a counterion.

To impede the rotation of the two thiazole rings upon oxidation and to impose a planar geometry on the DTDAF, *N*,*N'*-ethylene-bridged DTDAF **24** was prepared.[41] Using the in situ approach, a solution of TCNQ was added in the medium where the donor was formed.[83] A small amount of crystalline product was obtained, and X-ray structure determination revealed that the charge transfer complex had not formed with **24** but rather with a new donor **25** formed by intermolecular coupling of the starting
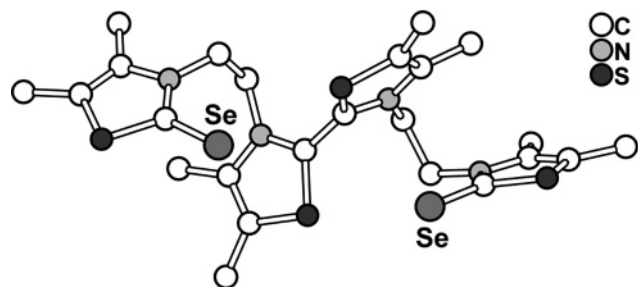
Figure 11. Molecular structure of the DTDAF 25^{2+} in (DTDAF 25)(TCNQ)$_3$ showing the nonplanarity of the donor core.

Figure 12. View of the molecular packing of (DTDAF **25**)-(TCNQ) projected in the ac plane showing the location of the TCNQ between two thiazoline-2-selones.

material instead of the expected intramolecular one (Scheme 27 and Figure 11). Nevertheless, this salt was interesting to investigate, since it is only the third example of a crystallographically characterized TCNQ salt of a DTDAF.

Scheme 27

The donor−acceptor ratio was one donor for three TCNQs, with two crystallographic distinct TCNQs arranged according to the sequence BAB, where the trimers of TCNQ are sandwiched between two thiazoline selone moieties of different donor cores (Figure 12). A ring-over-bond overlap was observed between TCNQ A and TCNQ B with a longitudinal slip and an interplanar separation of ≈3.3 Å, while an interplanar separation of ≈3.6 Å is observed between the thiazoline selone moiety with TCNQ B. The conformation of the donor core is reminiscent of what was observed for the hexamethyl DTDAF

dication 8-Me^{2+} in (hexamethyl DTDAF)(TCNQ)$_3$. Indeed, the DTDAF core has a nonplanar structure with the two thiazole 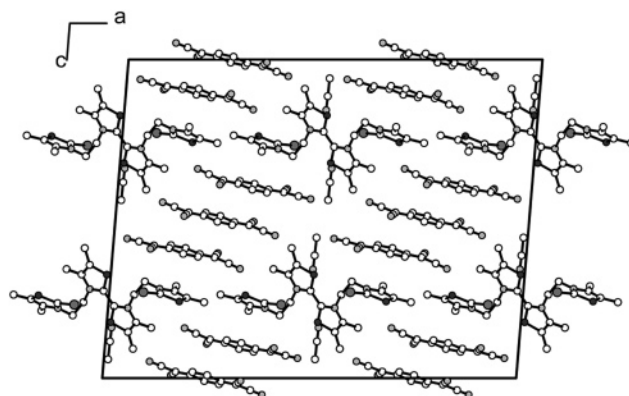rings twisted around the central C−C bond by an angle of 90.8°. Comparison of the bond lengths of the DTDAF skeleton with the one in hexamethyl DTDAF^{2+} tends to indicate that the donor is in its dicationic form (see Table 7). This was confirmed by the evaluation of the formal charges of the three TCNQs from the bond length variation where the values of −0.37 and −0.81 were found for TCNQ A and TCNQ B, respectively, giving a −2 charge for the BAB TCNQ trimer.

Polyoxometalates are inorganic clusters formed by the association of MO$_6$ octahedra, which have been used as components in molecular materials.[84] They also possess high electron acceptor capabilities and are therefore potential acceptors if faced with very good donor molecules. Air sensitive quasi-planar N,N'-phenylene-bridged DTDAF **17** was trapped in situ by simply adding a solution of polyoxometalate (Bu$_4$N)$_2$Mo$_6$O$_{19}$ in acetonitrile. Considering the redox potentials of the donor and the acceptor, the DTDAF **17** ($E_1 = -0.47$ V vs SCE) is spontaneously oxidized in the medium by the polyoxometalate ($E_1 = -0.32$ V vs SCE). Then, the less soluble salt was harvested as black single crystals. X-ray crystal structure analysis has been carried out and showed a stoichi-

Table 7. Bond Lenghts (Å) for Neutral, Radical Cation, and Dication DTDAF

|	8-Dipp	8-Me	17$^{+\bullet}$	3-Me^{2+}	8-Me^{2+}	20-Ph^{2+}	25^{2+}
a	1.344(4)	1.341(2)	1.37(1)	1.553(17)	1.469(4)	1.48(1)	1.492(7)
b	1.785(3)	1.779(2)	1.691(8)	1.677(10)	1.692(3)	1.710(7)	1.665(5)
	1.782(3)	1.762(2)	1.698(8)		1.689(3)		
c	1.426(3)	1.438(2)	1.38(1)	1.313(11)	1.316(4)	1.313(9)	1.345(6)
	1.428(3)	1.392(2)	1.39(1)		1.337(4)		
d	1.760(3)	1.764(2)	1.758(9)	1.757(10)	1.718(3)	1.713(8)	1.698(6)
	1.758(3)	1.769(2)	1.740(8)		1.714(3)		
e	1.399(4)	1.397(2)	1.42(1)	1.409(10)	1.396(4)	1.40(1)	1.361(6)
	1.395(4)	1.432(2)	1.40(1)		1.393(4)		
f	1.326(4)	1.339(2)	1.31(1)	1.366(13)	1.342(4)	1.350(9)	1.373(7)
	1.317(4)	1.329(2)	1.33(1)		1.351(5)		
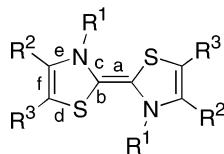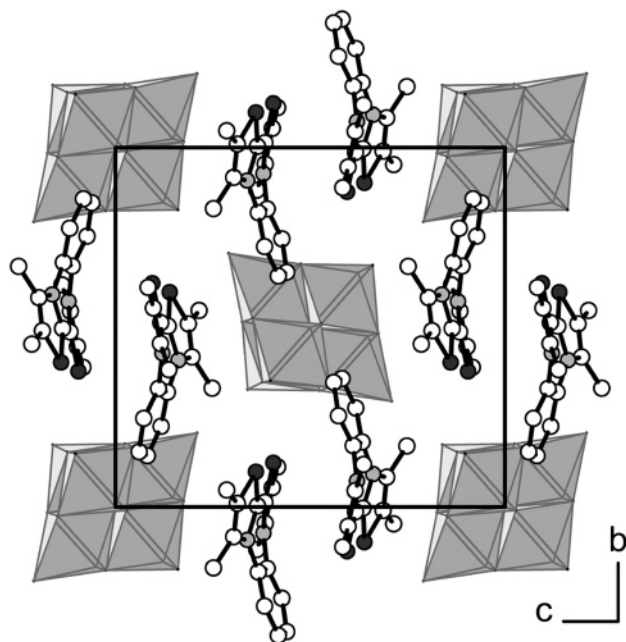
Figure 13. View of the unit cell of (DTDAF **17**)$_2$(Mo$_6$O$_{19}$).

ometry of two donors for one acceptor (Figure 13).[51] In this salt, the dianion Mo$_6$O$_{19}$$^{2-}$ is not reduced; therefore, the two DTDAFs were trapped as radical cation. This represents the first—and sole—crystallographically characterized example of a charge transfer salt involving the DTDAF radical cation. Donor molecules are not fully planar; the phenyl group is slightly bent out of the plane. They form isolated centrosymmetric dimers with no significant interdimer interaction (Figure 13). The ESR signal on single crystals has been investigated, and one single line due to DTDAF$^{+\bullet}$ radical cation has been observed. The bulk paramagnetism can be explained with a singlet (S = 0) triplet (S = 1) two level system with an antiferromagnetic interaction. Experimental susceptibility data are well-fitted with the Bleaney—Bowers formula (2J = 490 K) together with a Curie tail at low temperature, attributed to extrinsic Mo$_6$O$_{19}$$^{3-}$ species on the basis of EPR data.

The bond lengths in the TTF skeleton have often been used for the determination of the oxidation state of donors in charge transfer salts. Among the few crystalline examples of DTDAF, depending on the oxidation state, similar modifications of the bond lengths of the donor are observed. In Table 7, we summarize the bond lengths of the DTDAF core of all of the crystallographically characterized examples, as reference data for future comparisons. Upon oxidation, the central C=C double bond is lengthened while C—S and C—N bonds are shortened when compared with the neutral molecules (Table 7). This behavior finds its origin in the nature of the highest occupied molecular orbital (HOMO). The close analogy between the HOMO in hexamethyl-DTDAF and the HOMO in tetramethyl-TTF is represented in Figure 14. Bonding interactions between carbon atoms while antibonding interactions between the heteroatoms (nitrogen or sulfur) and carbon atoms are observed.
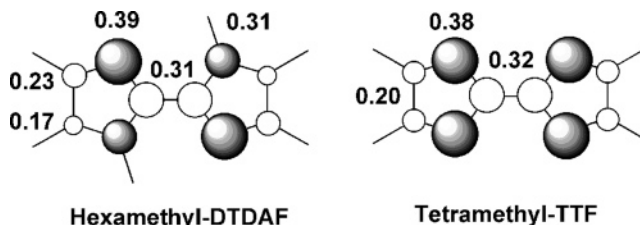

Figure 14.

5.2. Polymeric DTDAF

In recent years, conjugated aromatic and heteroaromatic polymers have been the subject of intense research due to their potential uses as light-emitting diodes (LED)s,[85] chemical sensors,[86] etc. Among the various polymeric backbones, the poly-(4,4′-dialkyl-2,2′-bithiazole) (PABT), essentially prepared by metal-catalyzed dehalogenative coupling, was also investigated.[87] Interestingly, *N*-methylation of these polymers alters dramatically the optical, electrical, and mechanical properties.[88,89] The *N*-methylated-PABT as well as the PABT are *n*-dopable polymers. Actually, the reduced *N*-methylated-PABT is nothing else than a poly DTDAF network (Scheme 28).

Scheme 28
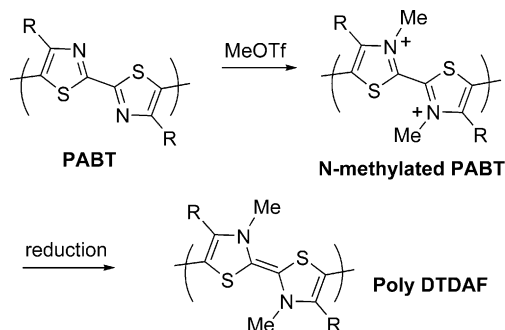
The electronic absorption showed important variations between the PABT, the *N*-methylated-PABT, and the *n*-doped *N*-methylated-PABT.[88,89] For instance, in the poly(dinonyl bithiazole) (R = nonyl), expected to be fairly planar, a red shift is observed up to 50% methylation, attributed to electronic effects. Contrariwise, with a higher degree of methylation, a blue shiftback to the $\lambda_{\max}$ of the original polymer is observed and attributed to steric hindrance forcing the rings out of planarity. The reduction of the *N*-methylated poly(dinonyl bithiazole) replaces the sharp peak observed at 442 nm by a broad absorption band that extends into the near-IR. Theoretical investigations were carried out in order to understand the changes in the electronic structure and polymer conformations upon *N*-methylation and reductive doping.[90] Full methylation of the PABT gives rise to nonconjugated polymers where the adjacent thiazolium rings are nearly orthogonal to each other, as it has been shown from geometry optimization on oligomers. Therefore, a blue shift is observed due to the torsion between the rings occurring upon the *N*-methylation. It should be noted that this polymer presents close analogy with

what was observed with *N*,*N*′-dimethyl-DTDAF dication. Reduction of this polymer induces a shift into the near-IR due to planarization of the polymeric backbone.

6. Concluding Remarks and Perspectives

In light of this review on the DTDAFs, it is clear that compared to TTFs, these derivatives appear to be a bit of an outsider in the field of molecular conductors. These unrecognized precursors of organic materials present striking properties as compared to their sulfur analogues the TTFs, all of them due to the presence of the nitrogen atom into the fulvalene skeleton. The less attractive one, which can be easily circumvented, was its instability toward oxygen. Once the chemist is aware of this difficulty, these derivatives offer wide possibilities. Their redox potential range can be easily modulated either through the donating or withdrawing electron ability of the substituents and, for instance, can be adapted to reduce several weak acceptors (C_{60}, polyoxometalates...) without the use of electrochemical techniques such as electrocrystallization. Even with four electron-withdrawing groups, which make these derivatives isolable under atmospheric conditions, these DTDAF are powerful donors. Taking advantage of the nitrogen atom, it is possible to control the geometry of the molecule at the various oxidation states by an outer bridge connecting the two thiazole moieties. Moreover, this rigidity brought to the fulvalene framework induces a large increase of the potential domain of stability for the cation radical species, which are responsible for the physical properties observed in molecular materials (conductivity, magnetism...). Some promising results have already been obtained. Optimization of the geometry and realization of novel molecular materials still have to be discovered to go in search of novel unsuspected qualities of this donor. Of particular interest will be the functionalization of the donor core by chalcogens; this type of modification has led in the TTF family (BEDT-TTF salts) to a large increase of the interactions between the donor moieties. Introduction of halogens or groups with a high potential for hydrogen bonding would also certainly induce novel architectures. Another development for the DTDAF could be also envisioned; *N*,*N*′-dimethyl-DTDAFs exhibit rapid and reversible conformational modifications upon oxidation. In the field of molecular machines based on molecular movements triggered by electron transfer,[91] these derivatives appropriately substituted could be a new model. Hopefully, this review will provide guidelines to newcomers in DTDAF chemistry.

7. Acknowledgments

8. References

(1) (a) Ferraris, J.; Cowan, D. O.; Walatka, V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125.
(2) Narita, M.; Pittman, C. U. *Synthesis* **1976**, 489.
(3) Krief, A. *Tetrahedron* **1986**, *42*, 1204.
(4) (a) Schukat, G.; Richter, A. M.; Fanghänel, E. *Sulfur Rep.* **1987**, 7, 155. (b) Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1993**, *14*, 245. (c) Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1996**, *18*, 1.
(5) (a) Andrieux, A.; Duroure, C.; Jérome, D.; Bechgaard, K. *J. Phys. Lett.* **1979**, *40*, 381. (b) Jérome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, *41*, L95.
(6) For comprehensive reviews on organic superconductors, see (a) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992. (b) Ishiguro, T.; Yamaji, K.; Saito, G. *Organic Superconductors*, 2nd ed.; Springer-Verlag: Berlin, 1998.
(7) Mizuno, M.; Garito, A. F.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 18.
(8) Wanzlick, H. W.; Kleiner, H. J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 65.
(9) Vorsanger, J. J. *Bull. Soc. Chim. Fr.* **1964**, 119.
(10) Metzger, J.; Larivé, H.; Dennilauler, R.; Baralle, R.; Gaurat, C. *Bull. Soc. Chim. Fr.* **1964**, 2857.
(11) Quast, H.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 800.
(12) Kluger, R. *Chem. Rev.* **1987**, *87*, 863.
(13) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719.
(14) Breslow, R.; Schumck, C. *Tetrahedron Lett.* **1996**, *37*, 8241.
(15) Lachmann, B.; Steinmaus, H.; Wanzlick, H. W. *Tetrahedron* **1971**, *27*, 4085.
(16) Castells, J.; López-Calahorra, F.; Ceijo, F.; Pérez-Dolz, R.; Bassedas, M. *J. Heterocycl. Chem.* **1986**, *23*, 715.
(17) Castells, J.; López-Calahorra, F.; Domingo, L. *J. Org. Chem.* **1988**, *53*, 4433.
(18) López-Calahorra, F.; Castells, J.; Domingo, L.; Martí, J.; Bofill, J. *Heterocycles* **1994**, *37*, 1579.
(19) Martí, J.; López-Calahorra, F.; Boffill, J. M. *J. Mol. Struct.* **1995**, *339*, 179.
(20) López-Calahorra, F.; Rubires, R. *Tetrahedron* **1995**, *51*, 9713.
(21) Çetinkaya, E.; Küçükbay, H. *Turk. J. Chem.* **1995**, *19*, 24.
(22) Chen, Y. T.; Barletta, G. L.; Haghjoo, K.; Cheng, J. T.; Jordan, F. *J. Org. Chem.* **1994**, *59*, 7714.
(23) Moteshareı, K.; Myles, D. C. *J. Am. Chem. Soc.* **1997**, *119*, 6674.
(24) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.
(25) Wanzlick, H. W.; Kleiner, H. J.; Lasch, I.; Füldner, H. U.; Steinmaus, H. *Liebigs Ann. Chem.* **1967**, *708*, 155.
(26) Takamizawa, A.; Hirai, K.; Hamashima, Y.; Sato, H. *Chem. Pharm. Bull.* **1969**, *17*, 1462.
(27) Wanzlick, H. W.; Kleiner, H. G.; Lasch, I.; Füldner, H. U. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 126.
(28) Vorsanger, J. J. *Bull. Soc. Chim. Fr.* **1966**, 1772.
(29) Quast, H.; Hünig, S. *Chem. Ber.* **1966**, *99*, 2017.
(30) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *Liebigs Ann.* **1997**, 365.
(31) Lemal, D. M.; Lovald, R. A.; Kawano, K. I. *J. Am. Chem. Soc.* **1964**, *86*, 2518.
(32) Vorsanger, H. *Bull. Soc. Chim. Fr.* **1967**, 2124.
(33) Friedrich, W.; Kehr, H.; Kröhnke, F.; Schiller, P. *Chem. Ber.* **1965**, *98*, 3808.
(34) Balli, H. *Angew Chem. Int. Ed.* **1964**, *3*, 809.
(35) Baldwin, J. E.; Branz, S. E.; Walker, J. A. *J. Org. Chem.* **1977**, *42*, 4142.
(36) Balli, V. H.; Grüner, H.; Maul, R.; Schepp, H. *Helv. Chim. Acta* **1981**, *64*, 648.
(37) Doughty, M. B.; Risinger, G. E. *Bioorg. Chem.* **1987**, *15*, 1.
(38) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1991**, *113*, 985.
(39) Bssaibis, M.; Robert, A.; Lemaguerès, P.; Ouahab, L.; Carlier, R.; Tallec, A. *J. Chem. Soc., Chem. Commun.* **1993**, 601.
(40) Koizumi, T.; Bashir, N.; Kennedy, A. R.; Murphy, J. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3637.
(41) Guérin, D.; Carlier, R.; Lorcy, D. *J. Org. Chem.* **2000**, *65*, 6069.
(42) Guérin, D.; Carlier, R.; Guerro, M.; Lorcy, D. *Tetrahedron* **2003**, *59*, 5273.
(43) Wahl, H.; Vorsanger, J. J. *Ind. Chim. Belge* **1967**, *32*, 139.
(44) Vorsanger, J. J. *Bull. Soc. Chim. Fr.* **1968**, 971.
(45) Washabaugh, M.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 674.
(46) Chen, Y. T.; Jordan, F. *J. Org. Chem.* **1991**, *56*, 5029.
(47) Kleiner, H. J. *Liebigs Ann. Chem.* **1969**, *724*, 221.
(48) Tormos, G. V.; Neilands, O. J.; Cava, M. P. *J. Org. Chem.* **1992**, *57*, 1008.
(49) Tormos, G. V.; Bakker, M. G.; Wang, P.; Lakshmikantham, M. V.; Cava, M. P.; Metzger, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 8528.

(50) Tormos, G. V.; Cava, M. P.; Metzger, R. M. *Polym. Mater. Sci. Eng.* **1995**, *72*, 296.

(51) Bellec, N.; Lorcy, D.; Robert, A.; Carlier, R.; Tallec, A.; Rimbaud, C.; Ouahab, L.; Clerac, R.; Delhaes, P. *Adv. Mater.* **1997**, *9*, 1052.

(52) Bellec, N.; Lorcy, D.; Boubekeur, K.; Carlier, R.; Tallec, A.; Los, S. Z.; Pukacki, W.; Trybula, M.; Piekara-Sady, L.; Robert, A. *Chem. Mater.* **1999**, *11*, 3147.

(53) Bellec, N.; Guérin, D.; Lorcy, D.; Robert, A.; Carlier, R.; Tallec, A. *Acta Chem. Scand.* **1999**, *53*, 861.

(54) Toplak, R.; Bénard-Rocherullé, P.; Lorcy, D. *Tetrahedron Lett.* **2002**, *43*, 3879.

(55) Casar, Z.; Lorcy, D.; Leban, I.; Majcen-Le Maréchal, A. *Acta Chim. Slov.* **2002**, *49*, 871.

(56) Bellec, N.; Lorcy, D.; Robert, A.; Carlier, R.; Tallec, A. *J. Electroanal. Chem.* **1999**, *462*, 137.

(57) Moses, P. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1974**, *96*, 945.

(58) Hünig, S.; Scheutzow, D.; Schlaf, H.; Quast, H. *Liebigs Ann. Chem.* **1972**, *765*, 110.

(59) Itoh, T.; Nagata, K.; Okada, M.; Yamaguchi, K.; Ohsawa, A. *Tetrahedron Lett.* **1992**, *33*, 6983.

(60) Itoh, T.; Nagata, K.; Okada, M.; Ohsawa, A. *Tetrahedron* **1993**, *49*, 4859.

(61) Goulle, V.; Chirayil, S.; Thummel, R. P. *Tetrahedron Lett.* **1990**, *31*, 1539.

(62) Jutzi, P.; Gilge, U. *J. Heterocycl. Chem.* **1983**, *20*, 1011.

(63) Nojima, M.; Nagao, G.; Kakeya, N.; Takagi, M.; Tokura, N. *J. Chem. Soc., Chem. Commun.* **1976**, 486.

(64) Baldwin, J. E.; Walker, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 596.

(65) Yamaguchi, K.; Itoh, T.; Nagata, K.; Okada, M.; Ohsawa, A. *Acta Crystallogr.* **1993**, *C49*, 1514.

(66) Giffard, M.; Alonso, P.; Garin, J.; Gorgues, A.; Nguyen, T. P.; Richomme, P.; Robert, A.; Roncali, J.; Uriel, S. *Adv. Mater.* **1994**, *6*, 298.

(67) Hünig, S.; Berneth, H. *Top. Curr. Chem.* **1980**, *92*, 1.

(68) Hünig, S.; Schlaf, H.; Kieblich, G.; Scheutzow, D. *Tetrahedron Lett.* **1969**, *27*, 2271.

(69) Hünig, S.; Scheutzow, D.; Schlaf, H. *Liebigs Ann. Chem.* **1972**, 126.

(70) Hünig, S.; Scheutzow, D.; Schlaf, H.; Pütter, H. *Liebigs Ann. Chem.* **1974**, 1436.

(71) Hurtley, W. R. H.; Smiles, S. *J. Chem. Soc.* **1926**, 2263.

(72) Hünig, S.; Kiesslich, G.; Quast, H.; Scheutzow, D. *Liebigs Ann. Chem.* **1973**, 310.

(73) (a) Scott, B. A.; La Placa, S. J.; Torrance, J. B.; Silverman, B. D.; Welber, B. *J. Am. Chem. Soc.* **1977**, *99*, 6631. (b) Hudhomme, P.; Le Moustarder, S.; Durand, C.; Gallego-Planas, N.; Mercier, N.; Blanchard, P.; Levillain, E.; Allain, M.; Gorgues, A.; Riou, A. *Chem. Eur. J.* **2001**, *7*, 5070.

(74) (a) Abboud, K. A.; Clevenger, M. B.; de Oliveira, G. F.; Talham, D. R. *J. Chem. Soc., Chem. Commun.* **1993**, 1560. (b) Chou, L.-K.; Quijada, M. A.; Clevenger, M. B.; de Oliveira, G. F.; Abboud, K. A.; Tanner, D. B.; Talham, D. R. *Chem. Mater.* **1995**, *7*, 530. (c) Ashton, P. R.; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951.

(75) Bssaibis, M. Ph.D. Thesis, University of Rennes, France, 1993.

(76) (a) Jørgensen, T.; Nasen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, 41. (b) Le Derf, F.; Mazari, M.; Mercier, N.; Levillain, E.; Richomme, P.; Becher, J.; Garin, J.; Orduna, J.; Gorgues, A.; Sallé, M. *Chem. Commun.* **1999**, 1417. (c) Le Derf, F.; Mazari, M.; Mercier, N.; Levillain, E.; Trippé, G.; Riou, A.; Richomme, P.; Becher, J.; Garin, J.; Orduna, J.; Gallego-Planas, N.; Gorgues, A.; Sallé, M. *Chem. Eur. J.* **2001**, *7*, 447.

(77) Yamashita, Y.; Suzuki, T.; Saito, G.; Mukaz, T. *Chem. Lett.* **1985**, *11*, 1759.

(78) Metzger, R. M.; Wang, P.; Wu, X. L.; Tormos, G. V.; Lorcy, D.; Shcherbakova, I.; Lakshmikantham, M. V.; Cava, M. P. *Synth. Met.* **1995**, *70*, 1435.

(79) Konarev, D. V.; Semkin, V. N.; Graja, A.; Lyubovskaya, R. N. *J. Mol. Struct.* **1998**, *450*, 11.

(80) Konarev, D. V.; Lyubovskaya, R. N.; Semkin, V. N.; Graja, A. *Mol. Mater.* **1998**, *11*, 35.

(81) Chappel, J. S.; Bloch, A. N.; Bryden, W. A.; Haxfeld, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.

(82) Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallogr.* **1982**, *B38*, 1193.

(83) Guérin, D. Ph.D. Thesis, University of Rennes, France, 2001.

(84) Coronado, E.; Gómez-García, C. J. *Chem. Rev.* **1998**, *98*, 273.

(85) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.

(86) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.

(87) (a) Yamamoto, T.; Suganuma, H.; Maruyama, T.; Kubota, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1613. (b) Nanos, J. I.; Kampf, J. W.; Curtis, M. D. *Chem. Mater.* **1995**, 7, 2232.

(88) Curtis, M. D.; Cheng, H.; Johnson, J. A.; Nanos, J. I. *Chem. Mater.* **1998**, *10*, 13.

(89) Politis, J. K.; Curtis, M. D.; He, Y.; Kanicki, J. *Macromolecules* **1999**, *32*, 2484.

(90) McClain, M. D.; Dudis, D. S. *Synth. Met.* **2001**, *116*, 199.

(91) See, for example, the special issue on Molecular Machines: *Acc. Chem. Res.* **2001**, *34*, 409.