A cation radical salt of an extended tetrathiafulvalene analogue with a difurylethylene spacer

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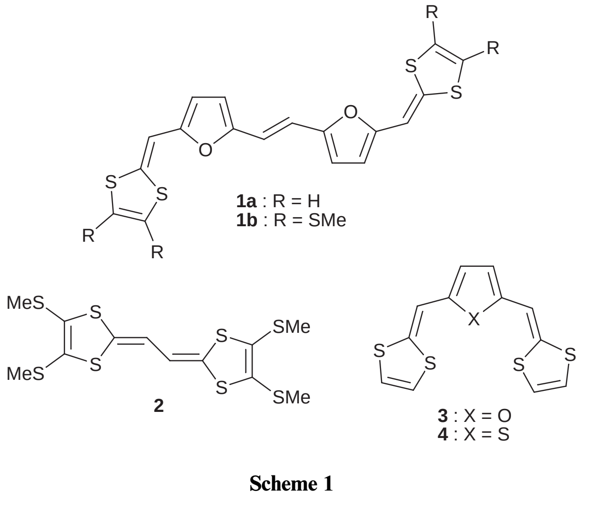
The X-ray structure of a single crystal of the neutral donor **1b** and its electrocrystallized cation radical salt, **1b** $\cdot$ ClO_4, have been analysed. Both the neutral and the oxidized states adopt a *syn* conformation stabilized by strong intramolecular interactions that allow the preservation of a planar conformation during the oxidation of **1b**.

Linearly extended systems built by insertion of a π-conjugated spacer between two donor groups (push-push) or between donor and acceptor ones (push-pull) represent a topic of great interest in the field of molecular conductors,[1] small band gap molecular semiconductors[2] and nonlinear optics.[3]

The conjugated spacer controls in part the behaviour of the molecule because it may allow extensive charge delocalization associated with a stabilization of the system. It has been shown recently that thienylenevinylene (TV) or furylenevinylene (FV) spacers combine efficient electronic transmission with a better thermal stability than ethylenic spacers.[4,5] In the field of molecular conductors of the tetrathiafulvalene (TTF) series, the spacers are end-capped with 1,3-dithiole-2-ylidene units.[6] Such linear extended hybrid TTF analogues have been widely explored because of (*i*) the stabilization of the radical cation expected from the better delocalization of the positive charge and (*ii*) the increased material dimensionality, which may result from the decreased charge density and increased π-interactions.

Owing to the difficulty in obtaining single crystals of radical cation salts or charge transfer complexes with such systems, very few materials of this family have yet been described, although many donors have been synthesized.[7] In this paper, we report the structure of furylenevinylene – TTF, **1**, in the neutral and oxidized states. The crystal structures are discussed by comparison with ethylenic, **2**,[8] furanic, **3**,[9] and thiophenic, **4**, analogues (Scheme 1).[9,10]



Scheme 1

Results and Discussion

The synthesis of the donors **1** and the structure of **1a**[5] have been described already. Single crystals of **1b** were obtained by slow evaporation of a $CHCl_3$ solution.

The X-ray structure of **1b** (Fig. 1) shows the *trans* configuration of the central linkage. As for **1a**, both ends of the molecule adopt a *syn* conformation stabilized by strong $S \cdots O$ intramolecular interactions. The nonbonded length $d = 2.99(2)$ Å is much shorter than the sum of the van der Waals radii ($r_S = 1.8$ Å and $r_O = 1.5$ Å) but longer than a covalent single bond length ($S{-}O = 1.75$ Å). The presence of electron-donating SMe groups produces a lengthening of the distance d from 2.88 Å for **1a** to 2.99 Å for **1b**. These results confirm those obtained by Hansen *et al.*[11] from similar intramolecular nonbonded $S \cdots O$ contacts. They observed that replacement of the electron-withdrawing SCOPh group by the electron-donating SMe leads to a shortening of *d*. As measured by the lengthening of the $S \cdots O$ nonbonded distance, the strength of the interaction decreases with the electron releasing power of the group borne by the 1,3-dithiole ring.

Electrocrystallization of **1a** and **1b** under galvanostatic conditions has been performed in the presence of ClO_4^- or BF_4^- as the counter anion. The main results are gathered in Table 1. Crystals having the formula **1** $\cdot$ ClO_4 or **1** $\cdot$ BF_4 grew to a size large enough for single crystal conductivity measurements (except for **1a** $\cdot$ BF_4 which gave a powder). The X-ray diffraction measurements were performed on these crystals but **1a** $\cdot$ CPO_4 was found to be twinned and the poor crystallographic quality of **1b** $\cdot$ BF_4 did not allow its structure to be solved. The 1 : 1 stoichiometry of **1b** $\cdot$ ClO_4 was determined from its X-ray structure.

The structure of **1b** $\cdot$ ClO_4 consists of two independent half-molecules, namely $\mathbf{1b}^{+\cdot}$ and $\mathbf{1b}'^{+\cdot}$ and one anion, ClO_4^-. As shown in Fig. 2, both centrosymmetrical cation radicals present a good planarity (except for one SMe group). Both ends of the molecules retain the stabilized δ *syn* conformation already discussed. The distances $d_1 = 2.729(6)$ Å and $d_2 = 2.776(6)$ Å are shorter than in the neutral molecule [$d = 2.99(2)$ Å], indicating a strengthening of the intramolecular $S \cdots O$ interaction in the oxidized state.

The key role of intramolecular interactions in the control of the planarity of both the neutral and the oxidized states has already been discussed for extended TTFs with thiophene (**4**) or furan (**3**) spacers.[9] In contrast, the ethylenic analogue of TTF (**2**), which presents a planar conformation in the neutral state, undergoes dramatic distortion upon oxidation.[8] Conse-

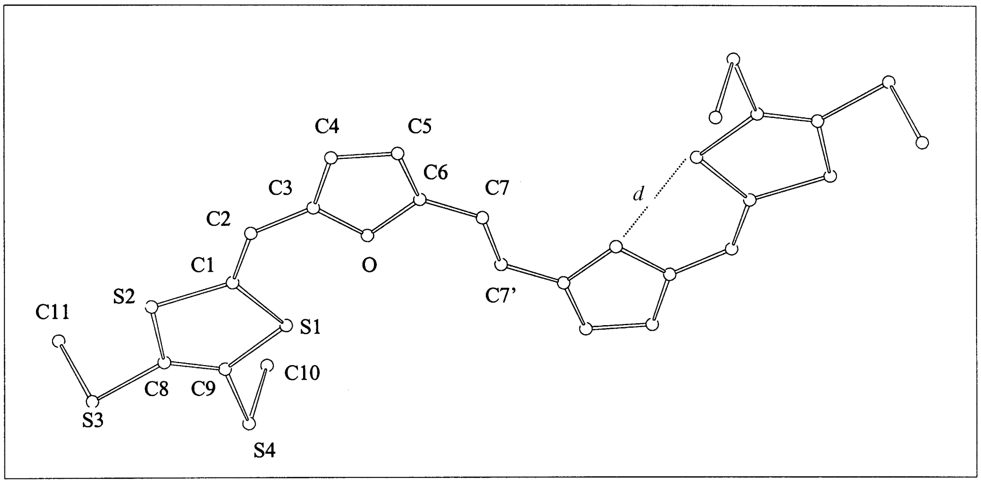


Fig. 1 View of the donor molecule **1b**

Table 1 Experimental conditions for the galvanostatic electrocrystallization of donors **1a** and **1b** on a platinum wire[a]

Donor	**1a**	**1a**	**1b**	**1b**
Anion	ClO_4^-	BF_4^-	BF_4^-	ClO_4^-
Results	Small crystals	Powder	Crystals	Crystals
Crystal size/mm	0.77 × 0.09 × 0.08		0.85 × 0.2 × 0.1	1.0 × 0.25 × 0.2
Conductivity/S cm^{-1}	4×10^{-3}	—	10^{-5}	10^{-4}

[a] Platinum wire of 0.5 mm diameter and 1.5 cm length. Solvent: CH_2Cl_2–EtOH (25.5 mL), $I = 0.8$ μA and $T = 2$ °C.

quently, the cation radicals $\mathbf{4}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ present the expected delocalized positive charge whereas in $\mathbf{2}^{+\bullet}$ the charge is mainly located on the central part of the molecule.[8]

Comparison of the bond lengths in $\mathbf{1b}^{+\bullet}$ and $\mathbf{1b}'^{+\bullet}$ shows marked differences (Table 2). The structure of $\mathbf{1b}^{+\bullet}$ is similar to that of the neutral compound **1b** with, in particular, a localized double bond on the central linkage u [with a slight lengthening from 1.31(2) Å in **1b** to 1.350(6) Å in $\mathbf{1b}^{+\bullet}$]. On the contrary, $\mathbf{1b}'^{+\bullet}$ presents an inversion of the lengths of bonds u and v, the central bond u becoming longer than v. For the

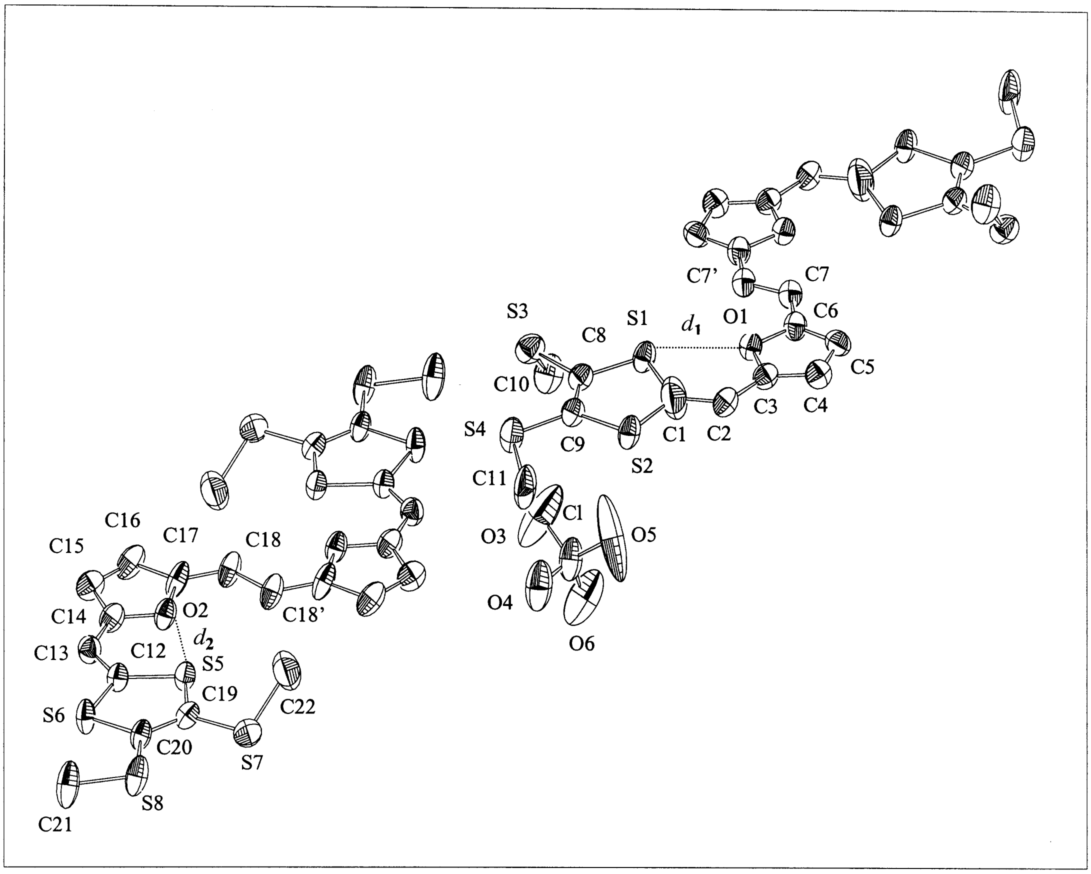
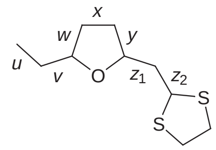


Fig. 2 Ortep view of the two cation radicals, $\mathbf{1b}^{+\bullet}$ and $\mathbf{1b}'^{+\bullet}$ and the anion ClO_4^-

Table 2 Bond lengths (Å) in the neutral molecule **1b** and the cation radicals $\mathbf{1b}^{+\cdot}$ and $\mathbf{1b'}^{+\cdot}$



	1b	$\mathbf{1b}^{+\cdot}$	$\mathbf{1b'}^{+\cdot}$
u	1.31(2)	1.350(6)	1.410(6)
v	1.42(2)	1.413(6)	1.375(6)
w	1.33(2)	1.386(7)	1.405(7)
x	1.37(2)	1.405(5)	1.361(6)
y	1.36(2)	1.364(6)	1.410(6)
z_1	1.41(2)	1.430(5)	1.384(5)
z_2	1.38(2)	1.345(6)	1.375(6)

furanic cycle, there is a lengthening of bonds w, y and a shortening of bond x. Moreover, as already observed in $\mathbf{3}^{+\cdot}$, the lengths of bonds z_1 and z_2 connecting the furan ring to the dithiole cycle are very similar. The more stable form expected for the radical cation of **1b** corresponds to the quinoidic structure **B** (Scheme 2) adopted by $\mathbf{1b'}^{+\cdot}$. Nevertheless, the structure of $\mathbf{1b}^{+\cdot}$ shows that the **A** form has a good stability too.

The structure of $\mathbf{1b}\cdot ClO_4$ is built up from columnar stacks of radical cations parallel to the [001] axis [Fig. 3(*a*)]. The steric interactions between the SMe groups are minimized by a shift of $\mathbf{1b}^{+\cdot}$ and $\mathbf{1b'}^{+\cdot}$ [Fig. 3(*b*)] and the average distance between radical cation planes is $d_i = 3.6$ Å [Fig. 3(*a*)]. Weak S···O intermolecular interactions with $d_3 = 3.55$ Å are observed [Fig. 3(*b*)].

Two-probe conductivity measurements performed on a single crystal gave values of 10^{-4}, 10^{-5} and 4×10^{-3} S cm^{-1} for $\mathbf{1b}\cdot ClO_4$, $\mathbf{1b}\cdot BF_4$ and $\mathbf{1a}\cdot ClO_4$, respectively. The higher conductivity of $\mathbf{1a}\cdot ClO_4$ can be related to an increase in the intermolecular interactions, due to the absence of steric hindrance between the SMe groups in the radical cation, thus favouring the intra-stack contacts.

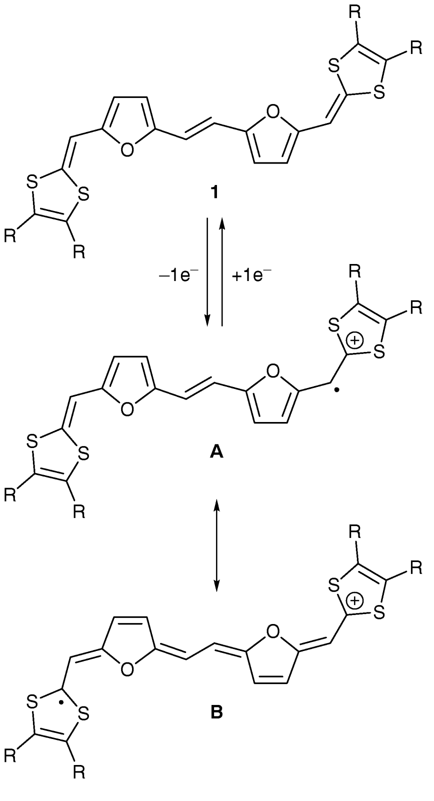
Conclusions

The X-ray structure of donor **1b** and its cation radical salt have been described. Both the neutral and oxidized molecules adopt a *syn* conformation stabilized by strong intramolecular interactions. In spite of a 1 : 1 stoichiometry, these salts show a non-negligible conductivity, which can be related to an electronic delocalization along the stack combined with an easy access to the dicationic state (bipolaron). Hence, an improvement of the conductivity may be expected for donors with a larger spacer, which stabilizes the bipolaron.

Experimental

Donors were dissolved in degassed solvent (Table 1) containing the electrolyte and placed in the anode compartment of a 50 mL H-shaped electrocrystallization cell, separated from the cathode compartment by a porous glass frit. A constant current was applied for 10–12 days.

Single crystals for X-ray crystallography were mounted on an Enraf-Nonius MACH3 diffractometer with graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation at $T = 294$ K. The data collections were performed with the ω/2θ scan technique. The crystal structures were solved by direct methods (SIR) and refined by full-matrix least-squares techniques using MolEN software. Non-hydrogen atoms were refined anisotropically for $\mathbf{1b}\cdot ClO_4$ whereas for **1b**, S and O atoms were refined anisotropically and C atoms isotropically. The positions of the hydrogen atoms were calculated from the Hydro program. The small size of crystal **1b** did not allow us to obtain enough data to achieve a high structural accuracy. Crystal data and experimental details are listed in Table 3. CCDC reference number for $\mathbf{1b}\cdot ClO_4$ and **1b** is 440/064.



Scheme 2

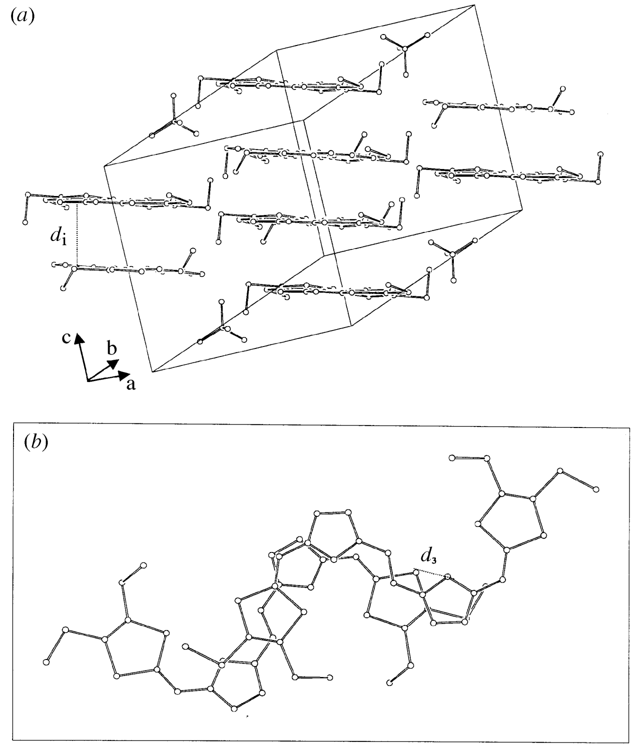


Fig. 3 X-Ray crystal structure of $\mathbf{1b}\cdot ClO_4$: (*a*) packing of the molecules and anions and (*b*) overlap mode of the cation radicals $\mathbf{1b}^{+\cdot}$ and $\mathbf{1b'}^{+\cdot}$.

Table 3 Crystallographic data

Compound	**1b** · ClO_4	**1b** · BF_4	**1b**
Crystal colour	Green	Green	Red
Crystal size/mm	1.0 × 0.25 × 0.2	0.85 × 0.2 × 0.1	1.0 × 0.2 × 0.05
Symmetry	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	$P2_1/n$
a/Å	10.959(8)	10.965(5)	5.182(3)
b/Å	12.237(7)	11.633(6)	10.357(2)
c/Å	12.851(4)	14.288(6)	23.654(1)
α/deg	108.50(4)	113.89(4)	90
β/deg	97.80(4)	90.18(5)	90.57(4)
γ/deg	115.07(5)	114.78(5)	90
U/Å^3	1405(3)	1480(4)	1269(8)
Z	2		2
Formula	$C_{22}H_{20}O_6S_8Cl$		$C_{22}H_{20}O_2S_8$
M	672.37		572.92
D_c/g cm^{-3}	1.59		1.50
F(000)	690		592
μ/mm^{-1}	0.743		0.710
θ_{min}, θ_{max}	2.5, 30		2.5, 25
h, k, l	$0 < h < 15$		$0 < h < 6$
	$-17 < k < 15$		$0 < k < 12$
	$-18 < l < 17$		$-28 < l < 28$
Unique data	8517		2371
Observed data, $I > 3\sigma(I)$	5872		557
No. of variables	355		90
R	0.080		0.054
wR	0.121		0.053

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