

Effect of heteroaromatic spacers on the structure and electrical properties of cation radical salts of tetrathiafulvalene analogs

Jean-François Favard,^a Pierre Frère,^{*a} Amédée Riou,^a Amina Benahmed-Gasmi,^b Alain Gorgues,^a Michel Jubault^a and Jean Roncali^a

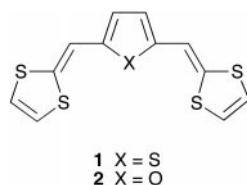
^aIngénierie Moléculaire et Matériaux Organiques, UMR 6501, Université d'Angers, 49045 Angers, France

^bLaboratoire de Chimie Organique, Université d'Oran, Es-Senia, 31000, Algérie

The X-ray crystal structure of single crystals of electrocrystallized cation radical salts of 2,5-bis(1,3-dithiol-2-ylidene)methyl)-thiophene and -furan **1** and **2** have been analysed. Both cation radicals adopt a *syn* conformation stabilized by strong intramolecular interactions. Bond length analysis reveals that the positive charge is delocalized over the whole molecule with enhanced delocalization for **2**^{•+} containing the less aromatic furan cycle. Whereas **2**^{•+} cation radicals are uniformly stacked along the *c* axis with interstack interactions, **1**^{•+} forms weakly interacting dimers stacked along the *b* axis. In agreement with an enhanced charge delocalization and increased dimensionality, **2**·BF₄ shows a conductivity *ca.* three orders of magnitude higher than **1**·ClO₄.

Since the discovery of the conducting properties of charge-transfer complexes and cation radical salts (CRSs) of the π donors of the tetrathiafulvalene (TTF) series,¹ much effort has been invested in the design of new π -donors by modification of the TTF framework.² The main objective of this research is the increased dimensionality and hence improved charge transport properties anticipated for the corresponding CRSs.^{3,4} A recent trend in this area consists of the insertion of a conjugated spacer between the two 1,3-dithiole rings in order to stabilize the cation radical state by the enhanced delocalization of the positive charge.³ Moreover, the decrease of the molecular charge density and the increase of π -interactions may allow better intra- and inter-stack contacts between the donor molecules and hence an increased dimensionality for the corresponding CRS. Based on these considerations, a new superconducting CRS has recently been obtained from a fused TTF with an ethylenic spacer.⁵ Linearly extended TTFs with a heterocyclic spacer have been synthesized almost simultaneously by four groups.⁶ However, the preparation and characterization of the corresponding CRSs have not yet been reported.

In this paper the preparation and X-ray diffraction structural characterization of two CRSs with thiophene **1** and furan **2** spacers are reported and the relationships between their structure and electrical properties are discussed.



Results and Discussion

Compounds **1** and **2** were synthesized using a known procedure.⁶ As already demonstrated, the insertion of a heterocyclic spacer into the TTF core results in a negative shift of the two oxidation potentials and in the decrease of their difference.⁶ Electrocrystallizations of **1** and **2** under galvanostatic condition have been performed in the presence of ClO₄⁻, BF₄⁻ and PF₆⁻ as counter anions. The main results are presented in Table 1. Green single crystals, namely **1**·ClO₄,

2·ClO₄ and **2**·BF₄, were grown whereas with the anion PF₆⁻ only powders were obtained. The 1:1 stoichiometry of **1**·ClO₄ and **2**·BF₄ was determined by X-ray crystallography. The quality of the single crystals of **2**·ClO₄ has not allowed us to obtain a structural resolution but the unit cell indicates that it is isostructural with **2**·BF₄.

As shown in Figs. 1 and 2, both cation radicals adopt a *syn* conformation stabilized by two strong intramolecular interactions, S...S for **1**^{•+} and S...O for **2**^{•+}, between the heteroatom of the middle heterocycle and a S atom of each 1,3-dithiole ring. The non-bonded lengths $d_1 = 3.11$; $d_2 = 3.06$ Å for **1**^{•+} and $d_1 = 2.956$; $d_2 = 2.926$ Å for **2**^{•+} are much shorter than the sum of the van der Waals radii ($r_{\text{WS}} = 1.8$ and $r_{\text{WO}} = 1.5$ Å) but larger than a covalent single bond length (S—S = 2.04 and S—O = 1.75 Å).

Such 1,5-intramolecular interactions between thiophene or furan rings and 1,3-dithiole rings have already been observed,^{7,8} in particular for the neutral donor **1** which adopts the same *syn* conformation.⁹ The similarity of the d_1 and d_2 lengths for **1** ($d_1 = 3.11$; $d_2 = 3.13$ Å) and **1**^{•+} shows that oxidation does not significantly affect the strength of these 1,5-intramolecular stabilizing interactions.

In contrast, marked differences are observed between **1** and **1**^{•+} in the bond lengths along the π -conjugated path and in particular for the exocyclic bonds x , x' and y , y' (Table 2). For the neutral molecule **1**, the lengths of the bonds x , x' and y , y' are consistent with localized double and single bonds respectively while the differences between C(sp²)–C(sp²) bond lengths Δl and $\Delta l'$ are close to the value expected for alternate single and double bonds (0.16 Å). Oxidation of **1** into **1**^{•+} produces a lengthening of bonds x and x' and a shortening of y and y' , resulting in a decrease of Δl and $\Delta l'$ and also in an inversion of the sign of Δl . The decrease in Δl and $\Delta l'$ provides conclusive evidence for extensive delocalization of the positive charge over the whole **1**^{•+} molecule (Scheme 1) while the inversion of Δl is consistent with an important contribution of the semiquinoid geometry (**B** form in scheme 1) in the cation radical.

Compared with **1**^{•+}, Δl and $\Delta l'$ for the furan analog **2**^{•+} decrease to *ca.* 0.01 and 0.02 Å. This bond length equalization suggests that the lower aromatic resonance energy of the furan ring allows a better delocalization of the positive charge over the whole cation radical **2**^{•+} than for **1**^{•+}. This enhanced delocalization is further favored by the better planarity of **2**^{•+}

Table 1 Experimental conditions for galvanostic electrocrystallization on platinum wire (diameter: 0.5 mm; length: 1.5 cm) of donors **1** and **2**. ACN: acetonitrile, EtOH: ethanol, THF: tetrahydrofuran

donor	1	1	1	2	2	2
anion	ClO_4^-	BF_4^-	PF_6^-	ClO_4^-	BF_4^-	PF_6^-
solvent	ACN (10 ml) EtOH (20 ml)	ACN (10 ml) EtOH (20 ml)	ACN	THF (20 ml) EtOH (10 ml)	THF (20 ml) EtOH (10 ml)	EtOH (10 ml)
current/ μA	1	1	0.8	1	1	0.5
$T/^\circ\text{C}$	0	0	2	5	5	5
results	crystals	small crystals	green solution and powder	crystals	crystals	green solution and powder

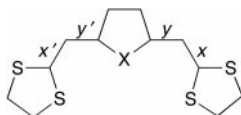


Table 2 Exocyclic bond lengths in Å of neutral molecule 1^0 and cation radicals $1^{+\cdot}$ and $2^{+\cdot}$

	x	x'	y	y'	$\Delta l = y - x$	$\Delta l' = y' - x'$
1 ($X=S$)	1.34(1)	1.28(1)	1.46(1)	1.45(1)	0.12	0.17
$1^{+\cdot}$ ($X=S$)	1.43 (2)	1.37(2)	1.37(2)	1.40(2)	-0.06	0.03
$2^{+\cdot}$ ($X=O$)	1.379(5)	1.370(5)	1.390(4)	1.392(4)	0.01	0.02

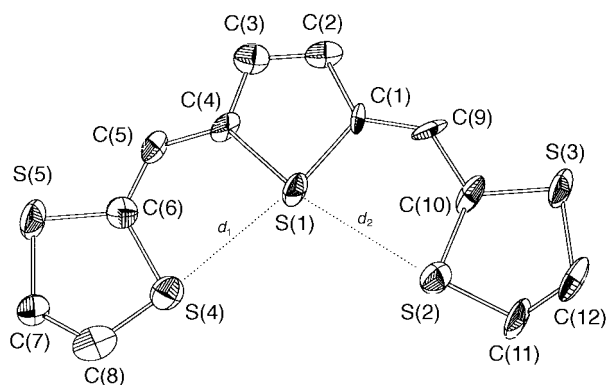


Fig. 1 ORTEP view of cation radical $1^{+\cdot}$

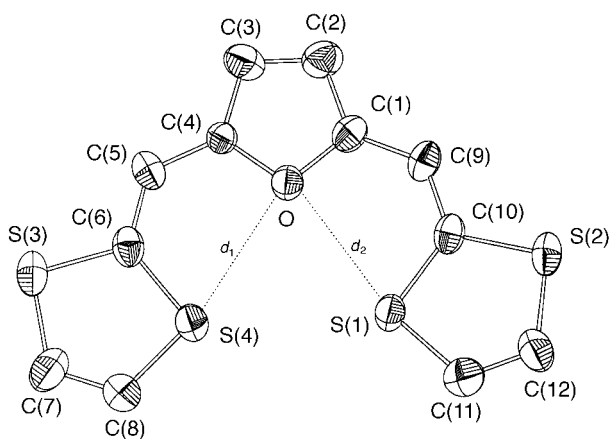
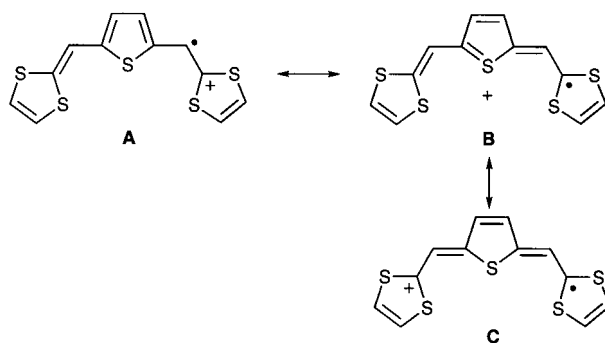


Fig. 2 ORTEP view of cation radical $2^{+\cdot}$

as shown by the decrease of the dihedral angles between the plane containing the middle heterocycle and those containing the 1,3-dithiolenyl rings from 1.9° and 1.3° for $1^{+\cdot}$ to 1.12° and 0.24° for $2^{+\cdot}$.

The packing of $1^{+\cdot} \cdot \text{ClO}_4^-$ and $2^{+\cdot} \cdot \text{BF}_4^-$ is characterized by a head-to-tail overlap of radical cations (Figs. 3 and 4). In $1 \cdot \text{ClO}_4^-$, dimers of cation radicals stack along the b axis. As shown in Fig. 3(b), several $\text{S} \cdots \text{S}$ intermolecular contacts are observed in the centrosymmetric dimer. The strongest interaction occurs between the sulfur atoms of thiophene with a



Scheme 1

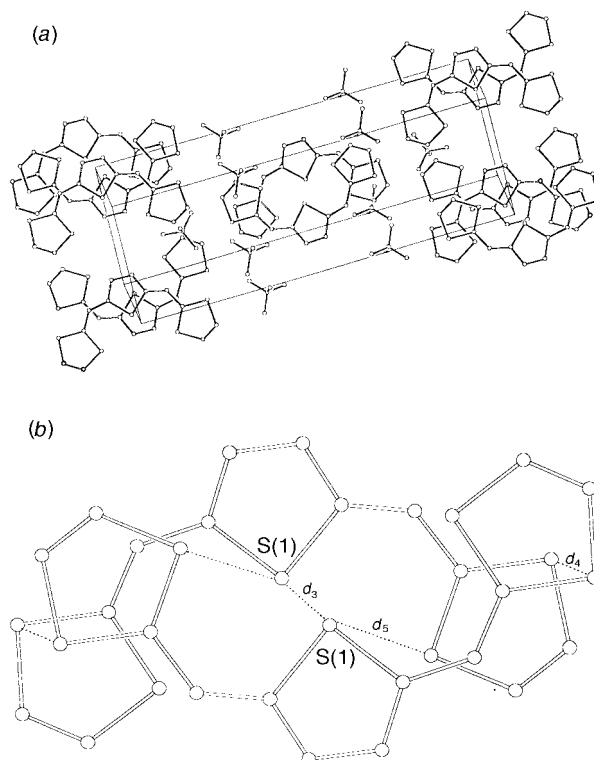


Fig. 3 X-Ray crystal structure of $1 \cdot \text{ClO}_4^-$: (a) packing of the molecules and anions and (b) overlap mode of cation radicals $1^{+\cdot}$ in the dimer

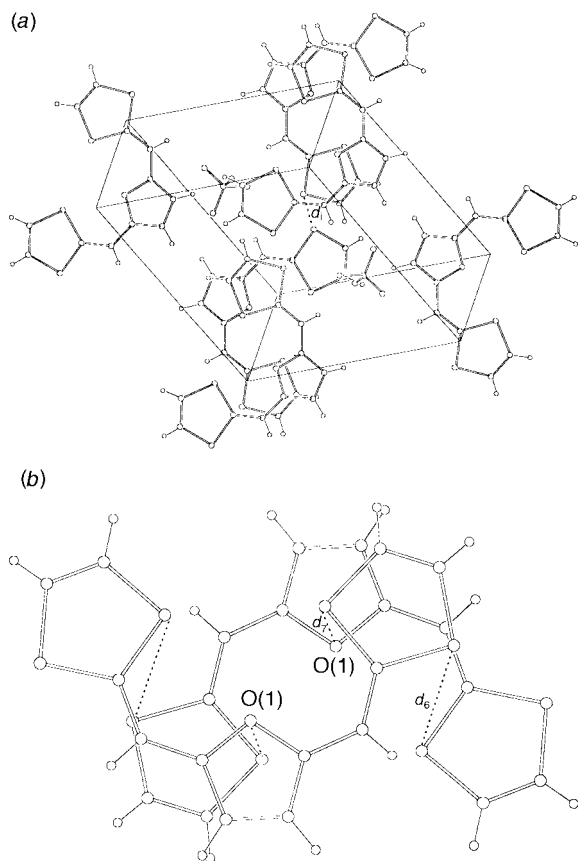


Fig. 4 X-Ray crystal structure of $2 \cdot \text{BF}_4$: (a) packing of the molecules and anions and (b) overlap mode of cation radicals 2^+

short distance $d_3 = 3.42 \text{ \AA}$. The sulfur atoms of the 1,3-dithiole rings are in weaker contact with $d_4 = 3.61$ and $d_5 = 3.76 \text{ \AA}$. Weak interactions are found between the dimers along the b axis (3.81 \AA) and no interstack contact is observed.

In sharp contrast, for $2 \cdot \text{BF}_4$ the cation radicals are uniformly stacked along the c axis with an overlap of the furan and 1,3-dithiole rings stabilized by regular $\text{S} \cdots \text{S}$ and weak $\text{S} \cdots \text{O}$ intermolecular interactions with $d_6 = 3.70$ and $d_7 = 3.35 \text{ \AA}$ respectively [Fig. 4(b)]. Interstack contacts are observed with $d_1 = 3.76 \text{ \AA}$ [Fig. 4(a)].

Two-probe conductivity measurements performed on a

single crystal only gave values of 7×10^{-5} , 4×10^{-2} and $10^{-2} \text{ S cm}^{-1}$ for $1 \cdot \text{ClO}_4$, $2 \cdot \text{ClO}_4$ and $2 \cdot \text{BF}_4$ respectively. The isomorphous crystals $2 \cdot \text{ClO}_4$ and $2 \cdot \text{BF}_4$ have analogous conductivities whereas the *ca.* three orders of magnitude larger value obtained for $2 \cdot \text{BF}_4$ in comparison with $1 \cdot \text{ClO}_4$ is in fair agreement with the enhanced charge delocalization and increased dimensionality indicated by X-ray data.

Conclusion

The first X-ray structures of cation radical salts of extended tetrathiafulvalenes with a thiophene and furan spacer have been described. Both cation radicals adopt the *syn* conformation stabilized by strong intramolecular interactions, previously observed for the neutral state. Compared to $1 \cdot \text{ClO}_4$, the better electronic delocalization over the whole radical cation 2^+ and above all the increased dimensionality of the crystal structure of $2 \cdot \text{BF}_4$ confer greater conductivity on this material. On the other hand, it is worth noting that the conductivity of $2 \cdot \text{BF}_4$ appears rather high for a CRS of 1:1 stoichiometry which should in principle behave as an insulator. This result suggests that the extension of charge delocalization allowed by the insertion of the heterocyclic spacer increases the probability of intermolecular charge transport. Work now in progress on more extended CRSs should permit us to confirm this hypothesis.

Experimental

Electrocrystallization

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 d.

X-Ray crystallography

Single crystals were mounted on an Enraf-Nonius MACH3 diffractometer with a graphite monochromator and Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation at $T = 294 \text{ K}$.

Data collection was performed with the $\omega/2\theta$ scan technique. The structures were solved by direct methods (SIR) and refined by full-matrix least-squares techniques using MOLEN software. Non-H atoms were refined anisotropically. The

Table 3 Crystallographic data

compound	$1 \cdot \text{ClO}_4$	$2 \cdot \text{BF}_4$	$2 \cdot \text{ClO}_4$
symmetry	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	7.096(5)	7.964(2)	7.929(2)
$b/\text{\AA}$	25.193(7)	10.341(2)	10.391(2)
$c/\text{\AA}$	9.765(4)	10.683(1)	10.820(3)
$\alpha(^{\circ})$	90	118.07(1)	117.97(2)
$\beta(^{\circ})$	105.08(6)	100.99(1)	101.45(2)
$\gamma(^{\circ})$	90	94.12(2)	94.28(2)
$V/\text{\AA}^3$	1685(2)	748.7(2)	757.1(4)
Z	4	2	2
formula	$\text{C}_{12}\text{H}_8\text{O}_4\text{S}_5\text{Cl}$	$\text{C}_{12}\text{H}_8\text{OS}_4\text{BF}_4$	$\text{C}_{12}\text{H}_8\text{O}_5\text{S}_4\text{Cl}$
M	411.97	383.26	395.90
$D_c/\text{g cm}^{-3}$	1.62	1.70	1.74
$F(000)$	836	386	402
μ/cm^{-1}	8.31	6.47	7.98
θ_{\min}	2	2	
θ_{\max}	28	30	
h, k, l	$0 < h < 9, 0 < k < 33, -12 < l < 12$	$0 < h < 11, -14 < k < 14, -15 < l < 15$	
data unique	4117	4634	
data observed, $I > 3\sigma(I)$	1229	3227	
no. of variables	199	223	
R	0.095	0.05	
R_w	0.121	0.07	

hydrogen atoms were found by Fourier difference in $2 \cdot \text{BF}_4$ and refined with fixed isotropic thermal parameters. In $1 \cdot \text{ClO}_4$, the positions of hydrogen atoms were calculated using the HYDRO program. Crystal data and experimental details are listed in Table 3 and data (excluding structure factors) for $1 \cdot \text{ClO}_4$ and $2 \cdot \text{BF}_4$ have been deposited at the Cambridge Crystallographic Data Centre. (See Information for Authors, Issue No. 1; quote reference 1145/63 in any request to the CCDC).

References

- (a) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M. H. Whangbo, *Organic Superconductors (Including Fullerenes)*, Prentice Hall, Englewood Cliffs, NJ, 1992; (b) *Organic Conductors. Fundamentals and Applications*, ed. J. P. Farges, Marcel Dekker, New York, 1994.
- (a) G. Shukat, A. M. Richert and E. Fanghanel, *Sulfur Rep.*, 1987, **7**, 155; (b) G. Shukat and E. Fanghanel, *Sulfur Rep.*, 1993, **14**, 245.
- M. Adam and K. Müllen, *Adv. Mater.*, 1994, **6**, 439.
- M. R. Bryce, *J. Mater. Chem.*, 1995, **5**, 1491.
- Y. Misaki, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1222.
- (a) U. Schöberl, J. Salbeck and J. Daub, *Adv. Mater.*, 1992, **4**, 41; (b) A. S. Benahmed-Gasmi, P. Frère, B. Garrigues, A. Gorgues, M. Jubault, R. Carlier and F. Texier, *Tetrahedron Lett.*, 1992, **33**, 6457; (c) T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. E. Niziurski-Mann, F. Jensen and J. Becher, *J. Am. Chem. Soc.*, 1992, **114**, 5035; (d) K. Takahashi, T. Nihira, M. Yoshifuji and K. Tomitani, *Bull. Chem. Soc. Jpn.*, 1994, **66**, 2330.
- (a) Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi and M. Sano, *J. Org. Chem.*, 1992, **57**, 5517; (b) Y. Misaki, T. Sasaki, T. Ohta, H. Fujiwara and T. Yamabe, *Adv. Mater.*, 1996, **8**, 804; (c) A. Ohta and Y. Yamashita, *J. Chem. Soc., Chem. Commun.*, 1995, 557; (d) A. Ohta and Y. Yamashita, *J. Chem. Soc., Chem. Commun.*, 1995, 1761; (e) A. Ohta and Y. Yamashita, *Heterocycles*, 1997, **1**, 263.
- T. K. Hansen, M. R. Bryce, J. A. K. Howard and D. S. Yffit, *J. Org. Chem.*, 1994, **59**, 5324; (b) E. H. Elandaloussi, P. Frère, A. Benahmed-Gasmi, A. Riou, A. Gorgues and J. Roncali, *J. Mater. Chem.*, 1996, **12**, 1859; (c) A. Benahmed-Gasmi, P. Frère, E. H. Elandaloussi, J. Roncali, J. Orduna, J. Garin, M. Jubault, A. Riou and A. Gorgues, *Chem. Mater.*, 1996, **8**, 2291.
- J. Roncali, L. Rasmussen, C. Thobie-Gautier, P. Frère, H. Brisset, M. Sallé, J. Becher, O. Simonsen, T. K. Hansen, A. Benahmed-Gasmi, J. Orduna, J. Garin, M. Jubault and A. Gorgues, *Adv. Mater.*, 1994, **6**, 841.

Paper 7/06948K; Received 25th September, 1997