

Protonated Tetrathiafulvalene: Preparation, Isolation and Crystal Structure of 2-(1,3-Dithiol-2-yl)-1,3-dithiol-1-ium Tetrafluoroborate

Michel Giffard,^a Pierre Frère,^a Alain Gorgues,^{* a} Amédée Riou,^a Jean Roncali^b and Loïc Toupet^c

^a *Laboratoire de Chimie Organique Fondamentale et Appliquée, Université d'Angers, 2 Bd Lavoisier, 49045 Angers Cedex, France*

^b *Laboratoire des Matériaux Moléculaires, CNRS UPR 241, 2 rue Henry Dunant, 94320, Thiais, France*

^c *Groupe Matière Condensée et Matériaux, URA 804, Bat. 11B, Faculté des Sciences de Rennes, 35042, Rennes Cedex, France*

The title compound has been isolated and is characterized by NMR and X-ray diffraction.

Recent years have witnessed the growing importance acquired by organic conductors in the fields of synthetic chemistry and solid-state physics. These materials include in fact two main classes of compounds. Conducting polymers, such as polyacetylene or polyaromatic systems are constituted of linearly conjugated chains whereas molecular conductors such as the cation radical salts of π -donors of the TTF series involve segregated stacks of donor molecules and counter-ions.

Although these two classes of compounds differ in their mechanical, electronic and electrochemical properties, their common feature lies in the fact that the appearance of metallic conductivity requires the formation of mixed-valence states. These states can be reached either chemically or electrochemically and this process is sometimes concomitant to the material growth, as in the case of electrogenerated conjugated polymers or electrocrystallized cation-radical salts.

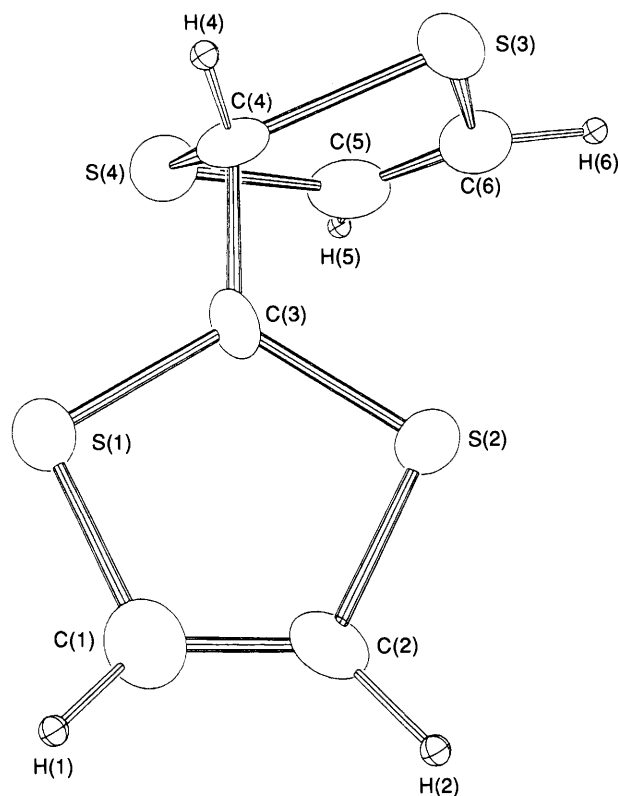
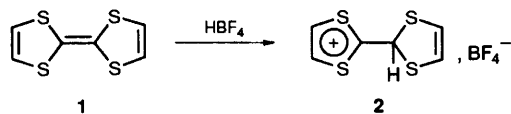


Fig. 1 ORTEP view of the cation $C_6H_5S_4^+$. Bond distances (\AA): S(1)–C(1) 1.70(1), S(1)–C(3) 1.676(9), S(2)–C(2) 1.69(1), S(2)–C(3) 1.681(9), S(3)–C(4) 1.82(1), S(3)–C(6) 1.75(1), S(4)–C(4) 1.82(1), S(4)–C(5) 1.74(1), C(1)–C(2) 1.34(1), C(3)–C(4) 1.50(1), C(5)–C(6) 1.30(2).

Until recently, it was generally admitted that in organic conductors, the electronic conductivity could be achieved only through oxidative or reductive doping. However, several recent works have shown that conjugated polymers or oligomers can acquire significant electronic conductivity by means of a non-oxidant protonic acid doping.¹ Although this process is rather well-documented in the case of conjugated polymers,¹ the situation is quite different for π -donors of the TTF **1** series.² As a matter of fact, although protonated TTF derivatives have been already proposed,³ until now, protonation has been spectroscopically detected only in the very particular case of solutions of a severely bent, highly reactive, cyclophane-type TTF derivative⁴ and to our knowledge, no protonated form of TTF has been isolated yet.

We report here the quantitative preparation of the protonated form of TTF which has been isolated as the corresponding tetrafluoroborate **2** and characterized by NMR spectroscopy and X-ray diffraction.

In a typical experiment, 2.5 mmol of **1** was dissolved in 10 cm^3 CHCl_3 , and 0.40 cm^3 (3 mmol) of a 54% ethereal HBF_4 solution diluted in 10 cm^3 CHCl_3 was added. The mixture was stirred for 30 min at room temp. and **2** was quantitatively obtained as a dark-red microcrystalline powder. Recrystallization (MeCN, -20°C) afforded fine needles m.p. $195\text{--}200^\circ\text{C}$. This compound readily reacts with water giving back TTF,

nevertheless it can be handled in ambient atmosphere for short periods.

The structure of **2** has been established by NMR spectroscopy in CD_3CN . The ^1H NMR spectrum exhibits three singlets with relative intensities 2 : 1 : 2, δ 6.38, (H5,H6), 6.62 (H4) and 8.94 (H1, H2). ^{13}C NMR 52.5 [$^1J_{\text{CH}}$ 164.0 Hz, C(4)], 117.7 [$^1J_{\text{CH}}$ 188.9 Hz, C(5), C(6)], 144.3 [$^1J_{\text{CH}}$ 200.3 Hz, C1, C2] and 211.0 [C(3)] [labelling is given in the ORTEP view (Fig. 1)]. In agreement with previous findings,⁴ the chemical shift of C(3) is consistent with a stronger localization of the positive charge at this carbon than in the case of the 1,3-dithiolium tetrafluoroborate.

Definitive proof of the structure of **2** has been obtained by X-ray diffraction.[†] As shown in Fig. 1, the added proton H(4) is clearly attached to C(4) [C(4)–H(4) distance: 0.8(1) \AA] while the C(3)–C(4) distance [1.50(1) \AA] lies in the range of carbon–carbon single bond lengths.⁵ On the other hand, the severely distorted structure of **2**, with the almost perpendicular two dithiolenyl units is in striking contrast with the nearly planar TTF geometry.⁶

These findings bring further support to the structure of the transient intermediates proposed to account for several acid-catalyzed reactions of substituted TTF derivatives such as isomerization around the central double bond,^{3a,b} or intramolecular cyclization.^{3c} On the other hand, one may question the possible role of protonated TTFs in the charge-transport process of some related materials,² even if such a question may seem strange in view of the severely bent structure of **2**.

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[†] Crystal data: $C_6H_5S_4BF_4$, $M_r = 292.17$, orthorhombic, space group, *Pbca*, crystal size $0.08 \times 0.10 \times 0.60$ mm, $a = 9.347(6)$, $b = 10.37(2)$, $c = 21.544(2)$ \AA , $V = 2088(4)$ \AA^3 , $Z = 8$, $D_c = 1.859$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 8.90$ cm^{-1} ; $T = 120$ K, 1937 reflections were collected. The limit of data collection was 2θ max = 50° . The structure was solved by a combination of direct methods and Fourier techniques and refined by full-matrix least squares analysis. Final discrepancy indices were $R_f = 0.063$ and $R_{wf} = 0.060$ for 888 independent reflections with $I > 3\sigma(I)$. Atomic scattering factors from international tables for X-ray crystallography (1974). All calculations were performed on a Digital MicroVAX 3100 computer with the MOLEN package.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.