ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2012, *57*(4-5), 457-462

Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary

[4+2] CYCLOADDUCTS BETWEEN ENANTIOPURE TETRAMETHYL-BEDT-TTF AND *ORTHO*-CHLORANIL: CONFORMATIONAL ISSUES IN THE SOLID STATE

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Received March 13, 2012

The unexpected formation, in electrocrystallization experiments, and structural characterization of enantiopure [4+2] cycloadducts between the enantiopure donors tetramethyl-bis(ethylenedithio)-tetrathiafulvalene (TMBEDT-TTF) as (*R,R,R,R*) and (*S,S,S,S*) enantiomers and *ortho*-chloranil are described. Single crystal X-ray analysis reveals the presence of axial and equatorial methyl groups within the same molecule in the solid state, and the establishment of intermolecular hydrogen bonds of $Cl\cdots H_3C_{eq}$ type.

INTRODUCTION

The introduction of chiral information in conducting salts of tetrathiafulvalene (TTF) derivatives,[1] a family of precursors extensively used in the preparation of molecular conductors[2] constitutes one of the strategies to achieve multifunctionnality in the field of molecular materials.[3] The phenomenon targeted in this approach is the electrical magneto-chiral anisotropy effect, which has been so far evidenced in the case of chiral carbon nanotubes,[4] but not in a chiral TTF based material. However, enantiopure conducting molecular systems are still rare.[1] In the case of TTF derivatives several conducting radical cation salts based on chiral TTFs (Scheme 1), such as the methylated BEDT-TTF (BEDT = bis(ethylenedithio)) DMBEDT-TTF[5] (DM = dimethyl) and TMBEDT-TTF (TM = tetramethyl),[6] or EDT-TTF-oxazolines,[7] have been synthesized.

In these examples of conducting salts the anions were achiral. However, the use of chiral anions might also allow the preparation of chiral radical cation salts, although the TTF precursor is achiral.[1,8] Recently, the use of the tris(tetrachlorobenzenediolato)phosphate(V) anion (TRISPHAT) (Scheme 2), provided with D_3 symmetry and configurational stability in solution,[9] in electrocrystallization experiments with BEDT-TTF,[10,11] enantiopure TMBEDT-TTF,[11] and racemic EDT-TTF-oxazolines[11] provided crystalline radical cation salts.

The TRISPHAT anion was present as a racemic mixture of Δ and Λ enantiomers, although the starting salt was Δ enantiopure. Thus, it seems that racemisation of the anion occurs under the electrocrystallization conditions. Another member of the tris(aryldiolato)phosphate(V) family of anions is the BINPHAT[12] (Scheme 2) in which a tetrachlorocatecholate is replaced by a binaphthol. The configuration at phosphorus is totally controlled by the binol ligand and, as a consequence, the anion exists in single

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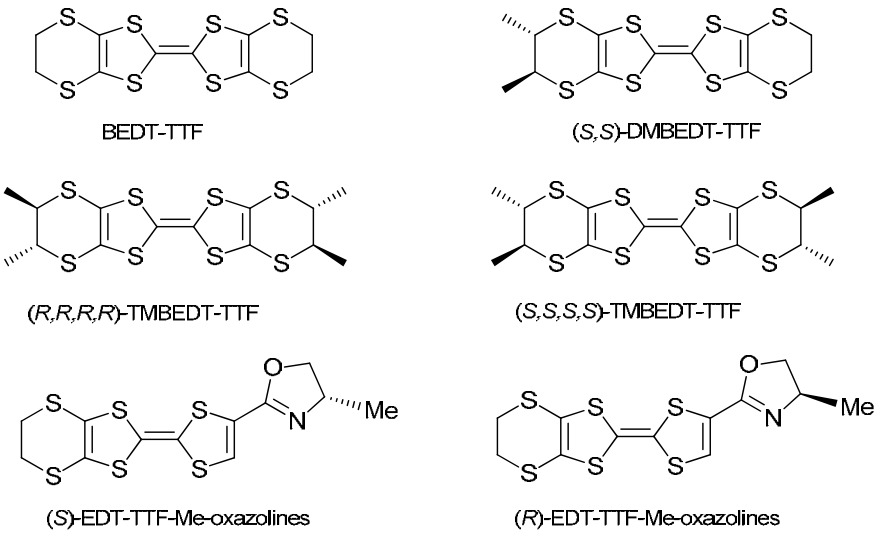
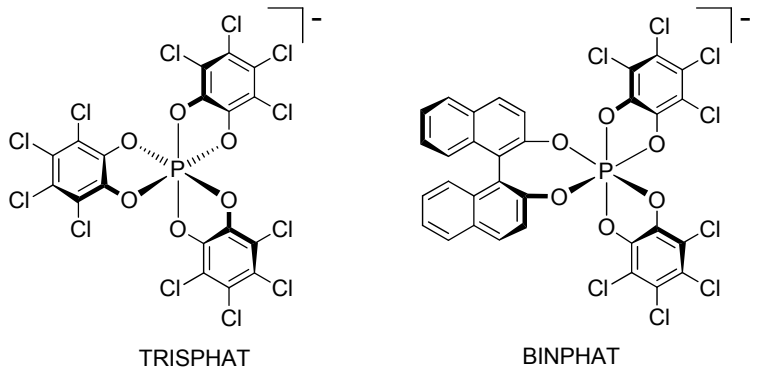
diastereomeric form *(i.e.* a (*S*)-configurated binol leads to the *Δ*-BINPHAT anion only). It tends however to be more fragile that the TRISPHAT anion due to the strain induced by the 7-membered ring. In our search of combining chiral TTF derivatives with chiral anions, we report herein on the electrocrystallization experiments results of the systems (*R,R,R,R*)-TMBEDT-TTF / BINPHAT and (*S,S,S,S*)-TMBEDT-TTF / BINPHAT.

FORMATION OF CYCLOADDUCTS AND THEIR X-RAY STRUCTURES

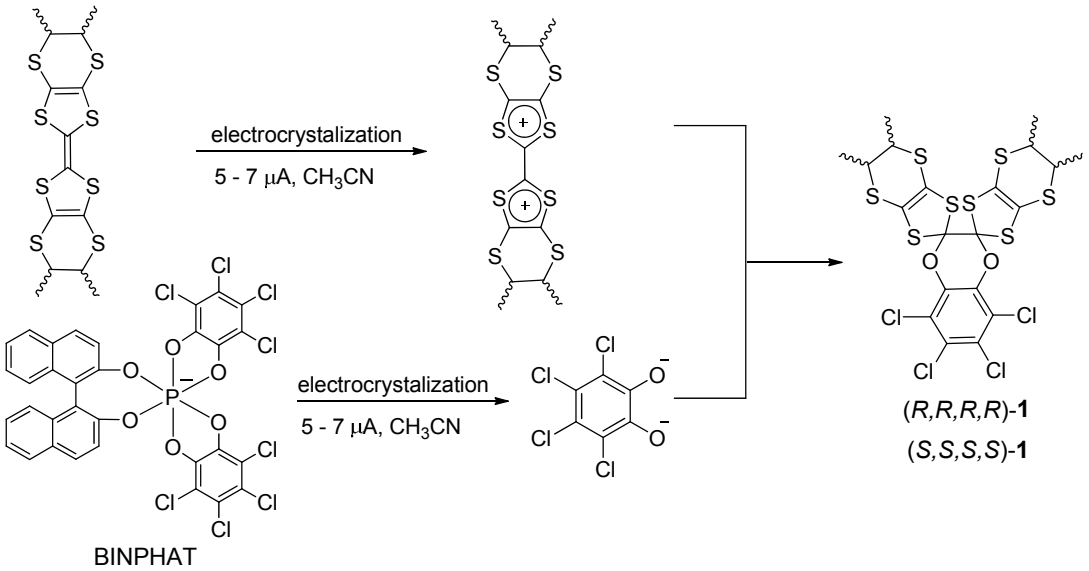
Electrocrystallization experiments of solutions of (*R,R,R,R*)-TMBEDT-TTF and (*S,S,S,S*)-TMBEDT-TTF in CH_3CN in the presence of [NBu_4][*Λ*-BINPHAT] as supporting electrolyte have been performed with the goal of preparing radical cation salts containing chiral donor and anion. After several days, two types of crystals, *i.e.* black plates and white prismatic blocks, have been collected in the anodic compartment of the cells. The former turned out to be, according to the single crystal X-ray analysis, the [TMBEDT-TTF][*rac*-TRISPHAT]·2CH_3CN (both enantiomers of TMBEDT-TTF) salts previously described.[11] Their formation can be possibly explained by exchange reactions taking place into solution, due to the weaker configurational stability of BINPHAT when compared to TRISPHAT. Formation of the white crystals (*R*)-**1** and (*S*)-**1** was more surprising, since their single crystal X-ray analysis shows a [4+2] cycloadduct type structure between TMBEDT-TTF and *o*-chloranil. A tentative mechanism for the formation of **1** is illustrated in Scheme 3, implying the initial generation of TTF dication and *o*-chloranilate dianion in the electrocrystallization conditions, followed by the formal [4+2] addition of *o*-chloranil on the central C–C bond of TTF, thus affording the enantiomeric [4+2] cycloadducts.



Scheme 1 – BEDT-TTF, chiral methylated BEDT-TTF, chiral TTF-Oxazoline donors.



Scheme 2 – TRISPHAT and BINPHAT anions. *Δ* configuration shown.



Scheme 3 – Formation of the enantiomeric cycloadducts **1**.

This type of cycloadduct is not unprecedented, since the reaction between the parent TTF and *o*-chloranil affords, beside the black charge transfer complex, the [4+2] cycloadduct, similar to our compound **1**,[13] upon longer stirring of the solution. It is clear therefore that this addition reaction occurs between the charged species.

^{1}H NMR spectra of **1** clearly show the typical resonances for the Me and CH protons, as doublets and multiplets, respectively. The structure of **1** has been definitely determined by single crystal X-ray structure analysis. Both enantiomers crystallize in the monoclinic system, chiral space group $P2_1$, but they are not isostructural. The (*R,R,R,R*) enantiomer, hereafter noted (*R*)-**1**, shows only one independent molecule in the unit cell. Interestingly, the arrangement of the Me groups is axial on one dithiane ring and equatorial on the other one (Ax/Eq conformation), while the junction of the three rings on the C–C bond imposes a deviation from planarity, which is of *Λ* type in this case (Fig. 1) with respect to the C_2 pseudo- axis C–C. The shortest intermolecular S···S contacts of 3.49 Å, below the sum of the van der Waals radii of two S atoms (3.70 Å), are observed in the packing diagram (Fig. 1) between a S atom of one dithiole ring (S3A) and a S atom of a dithiane ring (S1A) of a neighbouring molecule.

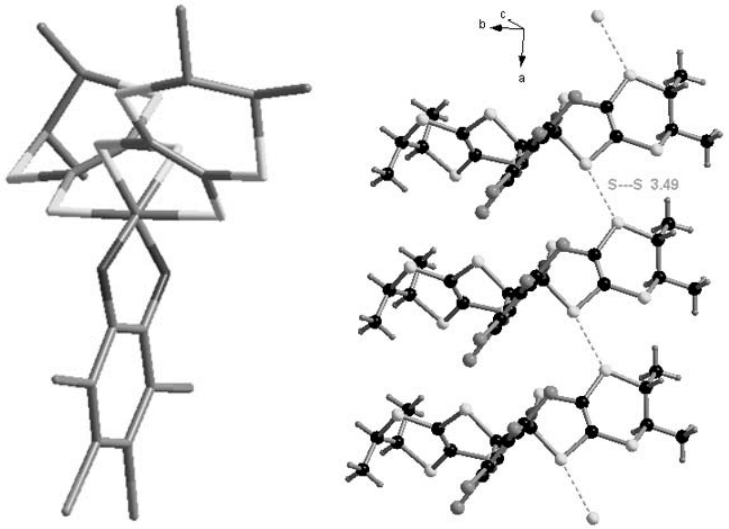


Fig. 1 – Crystalline structure of (*R*)-**1**, Ax/Eq conformation for the Me groups and *Λ* configuration for the C_2 axis; hydrogen atoms have been omitted (left). Intermolecular S···S contacts along *a* in the packing of (*R*)-**1** (right).

Establishment of weak hydrogen bonds of Cl···H_3C_{eq} type is observed (2.93 Å) in the *bc* plane, thus providing the formation of chains along the *b* direction (Fig. 2). Note that only the equatorial methyl groups are involved in these contacts.

Unexpectedly, since in general two enantiomers crystallize in a similar way in the same conditions, the crystal structure of (*S*)-**1** is different with respect to (*R*)-**1** in the sense that two independent molecules are now observed in the unit cell. In one of them the methyl groups show, as previously, Ax/Eq conformation, but *Δ* configuration along the C–C axis of the junction, while in the other one they adopt only axial positions (Ax/Ax) and *Λ* configuration along the C–C axis (Fig. 3).

Once again, hydrogen bonds of Cl···H_3C_{eq} type, even shorter (2.77 Å) than in the case of (*R*)-**1**, establish in the packing of (*S*)-**1** along the *b* direction, within the chains of *zig-zag* disposition between the Ax/Eq conformers. This leads to gaps in the packing which are filled by isolated Ax/Ax conformers (Fig. 4). No particularly short S···S intermolecular contacts are now observed in the packing.

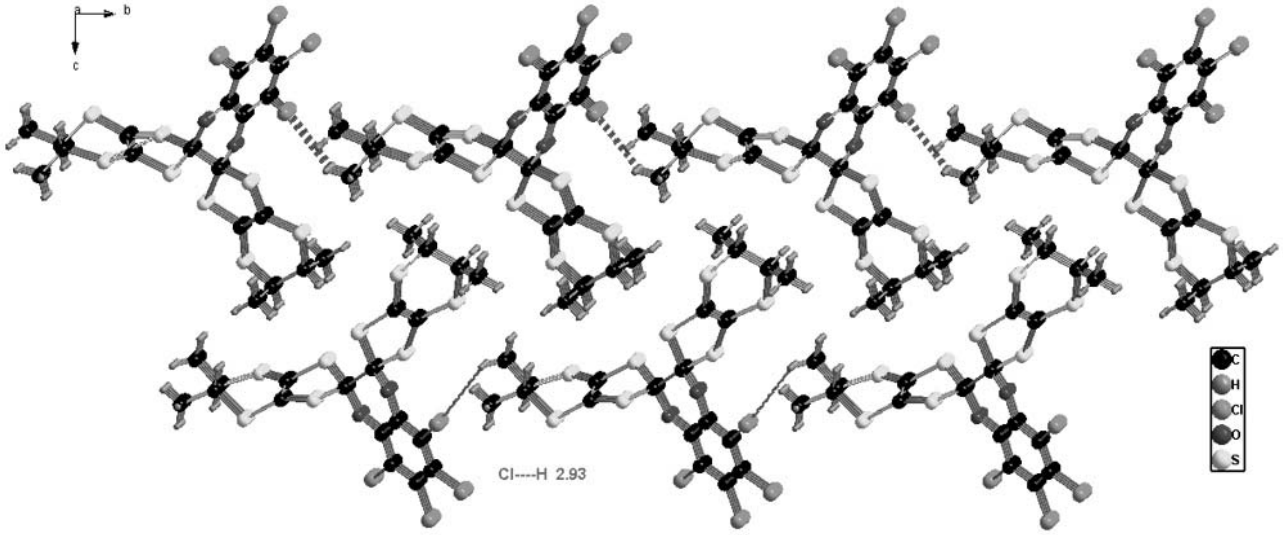


Fig. 2 – Packing diagram of (*R*)-**1** illustrating the formation of chains through Cl···H contacts.

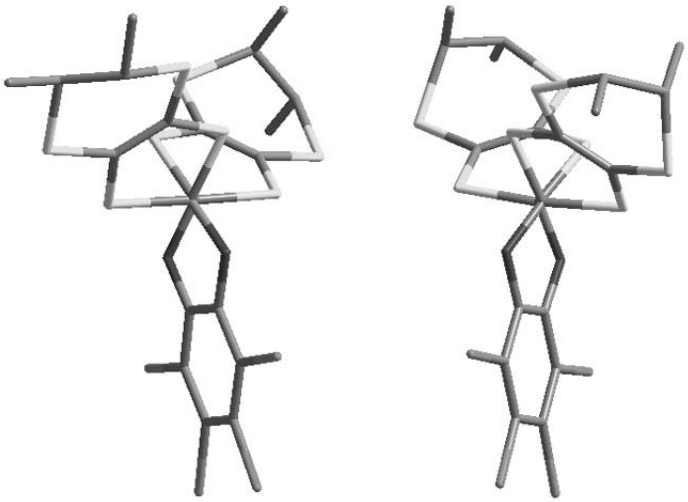


Fig. 3 – Crystalline structure of (*S*)-**1**, with Ax/Eq-*Δ* (left) and Ax/Ax-*Λ* (right) conformations for the methyl groups; hydrogen atoms have been omitted.

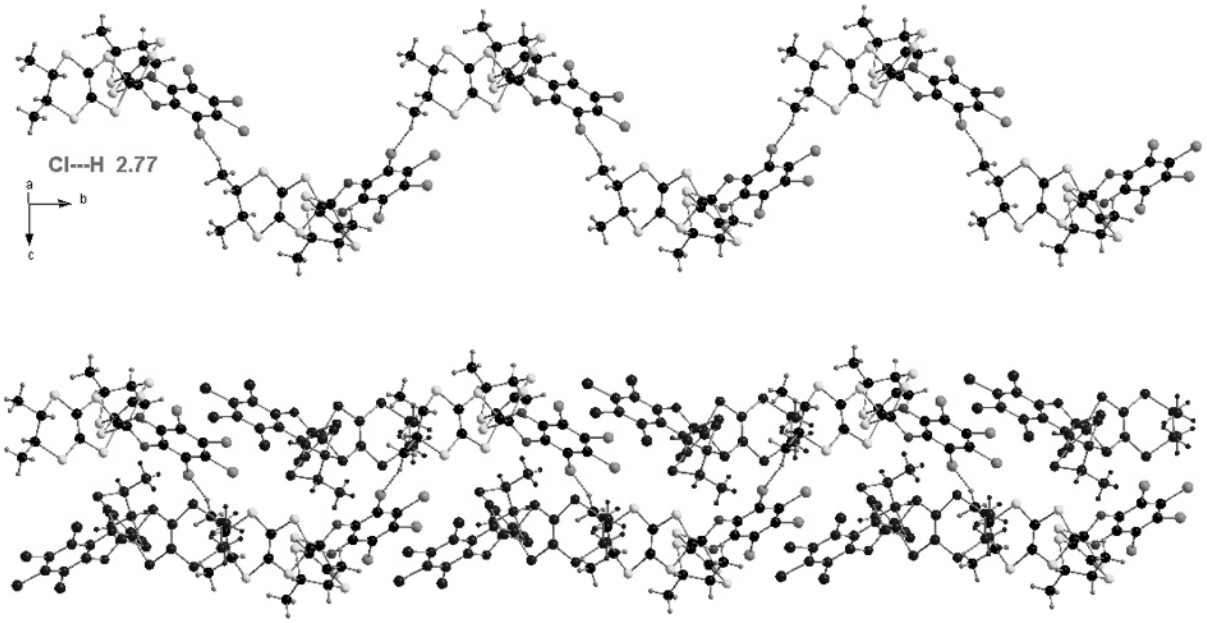


Fig. 4 – *Zig-zag* disposition of the Ax,Eq conformers in the packing of (*S*)-**1** (top), illustrating the formation of chains through Cl···H contacts. Gaps in the packing filled by Ax,Ax conformers represented in blue (bottom).

The fact that both axial and equatorial positions for the methyl groups are observed on the two dithiane rings of the same molecule in the crystal structures of (*R*)-**1** and (*S*)-**1** suggests that the energy difference between the Ax and Eq conformers is very low and the presence of one or another is very likely influenced by the intermolecular interactions established in the solid state, especially Cl···H hydrogen bonds (with equatorial methyl groups). This assumption is further supported by the presence, in the case of (*S*)-**1**, of only the axial conformer for one independent molecule, which is not involved in particularly short intermolecular contacts.

EXPERIMENTAL

Synthesis. (*R*)-1: 36 mg of [NBu_4][*Λ*-BINPHAT] were dissolved in 12 mL CH_3CN. In a half of this solution (*R,R,R,R*)-TMBEDT-TTF (5.0 mg) was added, and then the suspension was placed in the anodic chamber of the electrocrystallization cell, while the other half containing only the supporting electrolyte was poured in the cathodic compartment. Single crystals of the salt [(*R,R,R,R*)-TMBEDT-TTF][*rac*-TRISPHAT]·$2CH_3CN$,[11] as black plates (formed on the platinum electrode and also in solution), together with white prisms of (*R*)-**1** (formed only in solution) were grown at 20 °C over a period of 7 days, by applying a constant current of 5 μA for 3 days and then of 7 μA for 4 days. ^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm: 3.26 (m, 1H), 3.16 (m, 1H), 1.48 (d, 3H, ^3J = 6.6 Hz), 1.40 (d, 3H, ^3J = 6.6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm: 21.3 (CH_3), 21.8 (CH_3), 44.4 (CH), 45.1 (CH).
(*S*)-1: same conditions and amounts as previously. ^{1}H-NMR and ^{13}C-NMR are the same as for (*R*)-**1**.

X-Ray structure determinations. X-ray diffraction measurements were performed on a Bruker Kappa CCD diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2. [14] The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. A summary of the crystallographic data and the structure refinement is given in Table 1. CCDC reference numbers: 870744 for (*R*)-**1** and 870745 for (*S*)-**1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1

Crystallographic data, details of data collection and structure refinement parameters

	(*R*)-**1**	(*S*)-**1**
formula	$C_{20}H_{16}Cl_4O_2S_8$	$C_{20}H_{16}Cl_4O_2S_8$
M [gmol^{-1}]	686.61	686.61
T [K]	293(2) K	293(2) K
crystal system	Monoclinic	Monoclinic
space group	$P2_1$	$P2_1$
a [Å]	6.1025(4)	11.8979(6)
b [Å]	12.4708(13	20.380(3)

Table 1 (continued)

c [Å]	18.0508(13)	12.0771(9)
α [°]	90.00	90.00
β [°]	96.359(6)	109.079(5)
γ [°]	90.00	90.00
V [Å^3]	1365.27(19)	2767.5(4)
Z	2	4
ρ_{calcd} [gcm^{-3}]	1.670	1.648
μ [mm^{-1}]	1.065	1.051
goodness-of-fit on F^2	1.078	1.052
final R1/*w*R2 [I > 2σ(I)]	0.0328/0.0597	0.0403/0.0735
R1/*w*R2 (all data)	0.0469/0.0647	0.0723/0.0847

CONCLUSIONS

Electrocrystallization experiments with the enantiopure donors (*R,R,R,R*) and (*S,S,S,S*)-TMBEDT-TTF and the anion [NBu_4][*Λ*-BINPHAT] provided, unexpectedly, crystals of [4+2] cycloadducts between the donors and the *o*-chloranil unit. Single crystal X-ray analysis of these (*R*)-**1** and (*S*)-**1** adducts emphasize the presence of both axial and equatorial conformations for the methyl groups on the dithiane rings, the equatorial ones being involved in intermolecular Cl···H hydrogen bonds leading to the formation of chains. *Δ* and *Λ* configurations are observed with respect to the C–C axis of the adducts. Formation of **1** is very likely to occur through the reaction between oxidized species of the TMBEDT-TTF precursors and the *ortho*-chloranilate anion.

Acknowledgements: Financial support from the National Agency for Research (ANR, Project 09-BLAN-0045-01), the CNRS, and the French Ministry of Foreign Affairs through the Germaine de Staël (PHC 19137QF) project is gratefully acknowledged. Mr. Stéphane Grass is thanked for the preparation of the BINPHAT salt.

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