Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
Tetrahedron 61 (2005) 10935–10942

Tetrathiafulvalene-hydroxyamides and -oxazolines: hydrogen bonding, chirality, and a radical cation salt

Céline Réthoré, Marc Fourmigué* and Narcis Avarvari*

Laboratoire de Chimie, Ingénierie Moléculaire et Matériaux d'Angers, UMR 6200, Université d'Angers, UFR Sciences, Bât. K, 2 Bd. Lavoisier, 49045 Angers Cedex, France

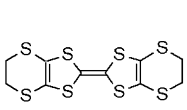
Received 20 July 2005; revised 25 August 2005; accepted 30 August 2005

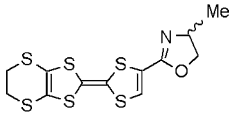
Available online 19 September 2005

Abstract—Racemic and enantiopure ethylenedithio-tetrathiafulvalene (EDT-TTF) derivatives featuring β-hydroxyamide or oxazoline (OX) groups bearing methyl or isopropyl substituents have been synthesized starting from the corresponding amino alcohols. Crystal structure analysis shows in the case of the racemic methyl-β-hydroxyamide donor the development of a unique hydrogen bond network, characterized by short C═O···H–O and N–H···O–H intermolecular distances. The enantiopure (*S*)-EDT-TTF-methyl-OX crystallizes in the monoclinic non-centrosymmetric space group $P2_1$, whereas the isopropyl counterparts, (*R*)-and (*S*)-EDT-TTF-isopropyl-OX, crystallize in the orthorhombic non-centrosymmetric space group $P2_12_12_1$. All of them adopt a *s-trans* conformation in which TTF and oxazoline units are coplanar. Electrocrystallization experiments with the racemic EDT-TTF-methyl-OX, in the presence of $(n\mathrm{Bu}_4)_2\mathrm{Mo}_6\mathrm{Cl}_{14}$ as supporting electrolyte, afford a radical cation salt, formulated as $[(\pm)\text{-EDT-TTF-methyl-OX}]_2\mathrm{Mo}_6\mathrm{Cl}_{14}$, in which the donors associate in strong dimers, which further stack along the b direction to form quasi-homochiral helix-like ribbons.

1. Introduction

The introduction of chirality within conducting molecular materials based on tetrathiafulvalene (TTF) derivatives, a well known class of organosulfur electron donors extensively studied in the search for molecular conductors and superconductors,[1] currently receives a growing interest, also encouraged by Rikken et al.'s recent report of electrical magnetochiral anisotropy in chiral carbon nanotubes.[2] This feature is in line with the quest for multifunctional molecular materials, a trend of much interest in contemporary materials science, aiming at combining in the solid state at least two physical properties, such as conductivity and optical activity.[3] The question of whether the chirality influences the electrical properties of TTF based radical cation salts had been previously addressed by Dunitz and others, but the lack of suitable enantiopure materials together with their racemic form did not allow deeper investigations.[4] Yet, structural differences between racemic and enantiomeric forms may occur, since enantiopure radical cation salts are expected to suffer less from structural disorder than the racemates, whose crystal structures may accommodate the enantiomers exchanging places. It is well established that structural disorder can strongly influence the electronic conductivity in molecular conductors,[5] therefore the chirality can already play a paramount role at this level. A straightforward strategy to introduce chirality within TTF based materials lies in the utilization of chiral TTF's as precursors for radical cation salts, although the complementary strategy, consisting of the use of chiral counter-ions with achiral donors can be envisioned, as recently described in the BEDT-TTF (bisethylenedithio-tetrathiafulvalene) salt with the chiral antimony (*L*)-tartrate dimer, $[\mathrm{Sb}_2(L\text{-tart})_2]^{2-}$.[6] The advantage of the former strategy, despite more synthetically-demanding efforts than for the second one, is that, once the synthesis of a chiral donor optimized, a large panel of anions, be they chiral or achiral, can be explored.


BEDT-TTF



EDT-TTF-OX

The first examples of enantiopure TTF derivatives were described by Dunitz and Wallis,[7] and since then other chiral TTF's were synthesized, most of them featuring a functionalized BEDT-TTF skeleton.[8] The latter, along with closely related donors, have been recently extensively

Keywords: Tetrathiafulvalenes; Chirality; Oxazolines; Crystalline structures; Electrocrystallization; Radical cation salts.
* Corresponding authors. Tel.: +33 2 41 73 50 84; fax: +33 2 41 73 54 05; e-mail addresses: marc.fourmigue@univ-angers.fr; narcis.avarvari@univ-angers.fr

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.08.104

surveyed by Wallis et al.[4] Moreover, enantiopure TTF derivatives containing chiral binaphthyl frameworks[9] or oxazoline rings[10] were also synthesized. The latter were tested as ligands in the catalytic allylic substitution reaction, showing though a rather modest catalytic activity.

In a recent communication we briefly described the straightforward synthesis of EDT-TTF (ethylenedithiotetrathiafulvalene) substituted with a chiral 4-methyloxazoline and a diphenylphosphino group.[11] The chirality provided by the oxazoline ring is perfectly controlled and easily introduced in the synthesis by the use of racemic or enantiopure amino alcohols. By synthesizing the EDT-TTF-Me-Oxazolines (EDT-TTF-OX), our purpose was to access a class of chiral donors, which could serve as precursors for chiral molecular materials. Indeed, this strategy proved to be highly promising for future developments, since we succeeded in preparing the first complete series of mixed-valence metallic salts based on chiral tetrathiafulvalenes bearing the (*R*)-, (*S*)-, or racemic (±)-methyl-oxazoline heterocycle and the AsF_6^- monoanion. The single crystal conductivity for the enantiopure salts was one order of magnitude higher than that of the racemic one, very likely because of the structural disorder observed in the latter.[12] In the present paper, we describe the detailed synthesis and characterization of chiral EDT-TTF-β-hydroxyamides and -oxazolines, in methyl and isopropyl series, in their racemic and (*R*) and (*S*) enantiopure forms. In depth analyses of crystal structures of racemic Me-hydroxyamide, enantiopure (*S*)-Me-oxazoline and (*R*) and (*S*)-*i*Pr-oxazolines are presented, along with that of a radical cation salt of racemic EDT-TTF-Me-oxazoline with the $Mo_6Cl_{14}^{2-}$ anion, obtained upon electrocrystallization.

2. Results and discussion

In order to introduce a chirality center on the oxazoline ring, our first choice to use a methyl substituent was motivated by the concern to have a minimum steric bulk, provided by the redox inert oxazoline part of the donor, in the radical cation salts of EDT-TTF-OX. This feature would favor a maximization of π–π overlap and van der Waals intermolecular interactions in the solid state. Secondly, in a parallel series of donors, an isopropyl substituent was used instead of methyl, in order to gain in solubility, but also to insure a steric protection for potential catalytic applications.

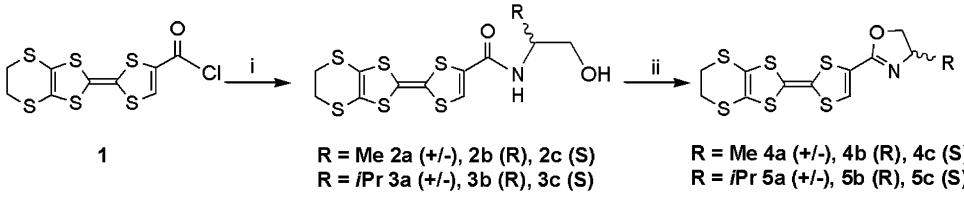
2.1. Synthesis

It is well established that EDT-TTF-COCl (**1**) smoothly reacts with primary amines to afford in good yields secondary amides.[13] Paralleling this strategy, two racemic (±) or enantiopure (*R*) and (*S*) amino alcohols, namely alaninol and valinol, were reacted with **1**, and, after stirring at room temperature for up to 12 h and chromatographic work up, the corresponding EDT-TTF-β-hydroxyamides **2a–c** and **3a–c** were isolated and characterized by spectroscopic methods and elemental analysis (Scheme 1). An X-ray crystal structure analysis was undertaken for compound **2a** (vide infra). Note these are the first examples of TTF's bearing both amide and alcohol functional groups, whereas numerous homofunctional derivatives of either amide,[13,14] thioamide[15] or alcohol[16] type were described so far. Subsequently, cyclization reactions in the presence of methanesulfonyl chloride (MsCl) and triethylamine were performed on β-hydroxyamides to yield the series **4a–c** (methyl) and **5a–c** (isopropyl) of (±), (*R*) and (*S*) EDT-TTF-oxazolines (EDT-TTF-OX). All analytical data and elemental analyses are in good agreement with the proposed structures. Suitable single crystals for X-ray analysis were obtained for the enantiopure donors **4c**, **5b** and **5c**.

2.2. X-ray crystal structures of donors

Suitable single crystals for the β-hydroxyamide **2a** were obtained upon recrystallization in ethyl acetate. The donor crystallizes in the monoclinic system, space group $P2_1/c$, with one independent molecule in the unit cell. As expected for a racemic mixture, both enantiomers, related to each other through the inversion center, are present in the structure. Selected bond lengths are listed in Table 1.

All values are typical for a neutral TTF, which, in this case, is moderately folded along both S···S hinges, that is, 15.33(18)° for S1···S2 and 19.9(3)° for S3···S4, as often encountered within crystalline structures of such neutral donors. The amide group is coplanar with the TTF unit, and disposed in an antiparallel manner with respect to C7=C8 and C9=O1 double bonds, as evidenced in Figure 1. Certainly, the most peculiar feature in the crystalline structure of **2a** is the hydrogen bond network established thanks to amide and alcohol groups. As observed for another β-hydroxyamide,[17] both functionalities participate as hydrogen bond donor and acceptor groups, with the carbonyl oxygen atom O1 acting as acceptor towards the alcoholic proton H2 and the amidic proton H1 as donor towards the alcoholic oxygen atom O2. The consequence of the balance between these requirements and the typical intermolecular S···S van der Waals contacts and stacking tendency of TTF type derivatives, is the organization of the donors in infinite ladders along a, through two types of hydrogen bond motifs (Fig. 1). Indeed, according to M. Etter's nomenclature,[18] one can identify $R_2^2(14)$ and $R_2^2(10)$ rings, characterized by short and rather linear hydrogen bonds of C=O···H–O and N–H···O–H type, respectively.



Scheme 1. Reagents and conditions: (i) (±), (*R*) or (*S*)-alaninol for **2a–c** and valinol for **3a–c**, NEt_3, THF, 12 h, rt; (ii) NEt_3, THF, MsCl at 0 °C, then 20 h at 50 °C.