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Bis(dithiomethyl-tetrathiafulvalene) with two phenyl-phosphino bridges

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ABSTRACT

The single crystal X-ray structure of the precursor dithiomethyl-tetrathiafulvalene $(MeS)_2TTF$ is reported, together with theoretical calculations at DFT level, which afforded two energy minima corresponding to *cis* and *trans* orientations of the thiomethyl substituents. The bis(tetrathiafulvalene) reaction of this TTF derivative followed by the reaction with phenyldichlorophosphine provides a new rigid bis(tetrathiafulvalene [TTF]) containing a 1,4-dihydro-1,4-diphosphinine ring between the two redox active units. Its solid-state structure, determined by single crystal X-ray diffraction analysis, shows the coexistence of both *cis* and *trans* isomers. Cyclic voltammetry measurements are in accordance with the existence of a communication between the two TTFs, as illustrated by the splitting of the oxidation waves.

1. Introduction

Tetrathiafulvalenes (TTF) and functional derivatives represent a well-known wide family of electroactive sulfur rich compounds [1], extensively used for various applications in molecular electronics and optoelectronics [2]. For many of these applications, the occurrence of multiple redox states is an important prerequisite. One of the straightforward strategies to address this issue is the use of dimeric TTF, in which, depending on the degree of the through-bond or through-space interactions between the redox active units, intramolecular mixed valence species can be evidenced in solution and/or in the solid state [3]. A particularly interesting family of bis(TTF) is that containing either one heteroatomic linker connecting the TTF moieties in close vicinity, such as the series $X(TTF)_2$, with X = S or Se [4], Te [5], PPh, $SiMe_2$ or Hg [6], Me_2Si–$SiMe_2$ [7], and SbMe [8], or two heteroatomic bridges as in the rigid derivatives $X_2(TTF)_2$, with X = S [9], Te [10], PPh [11], $SiMe_2$ and $GeMe_2$ [12] (Scheme 1).

The fused derivatives $(o\text{-DMTTF})_2(SiMe_2)_2$, $(o\text{-DMTTF})_2(GeMe_2)_2$ [12], and $(o\text{-DMTTF})_2(PPh)_2$ [11] have been described by us, together with the $(o\text{-DMTTF})_2(S{=}PPh)_2$ compound and coordination bimetallic complexes based on the last 1,4-dihydro-1,4-diphosphinine system [13]. In these compounds we have isolated, in solution or solid state, mixed valence species and demonstrated by spectroscopic and theoretical investigations extensive electron delocalization over both TTF units. One of the possible modifications of this type of rigid dimeric system consists of the variation of the lateral substituents on both TTFs, while keeping the same heteroatomic bridges, in order to extend the scope of these valuable precursors. We have thus decided to replace the lateral methyl substituents by thiomethyl ones in the bis(TTF)-diphosphinine fused system, since it is known that additional sulfur atoms attached to the TTF skeleton can engage in intermolecular S···S contacts in the solid state. Moreover, the thiomethyl substituents are expected to insure a better solubility of the rigid system. We describe herein the synthesis and single crystal X-ray structure of the bis(TTF) $[(MeS)_2TTF]_2(PPh)_2$, preceded by the description of the solid state structure and a theoretical study of the precursor $(MeS)_2TTF$.

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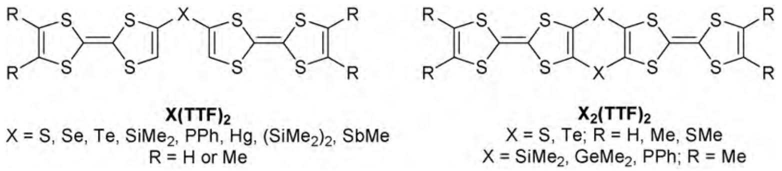
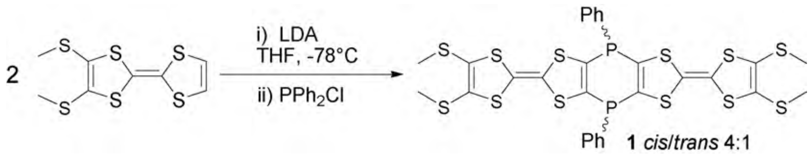


Scheme 1.



Scheme 2. Synthesis of **1**.

2. Results and discussion

2.1. *Structural and theoretical investigations on the dithiomethyl-tetrathiafulvalene precursor*

The precursor we have used for the preparation of the bis(TTF) system was the dithiomethyl-tetrathiafulvalene (MeS)$_2$TTF (Scheme 2), prepared using the published procedure involving the phosphite mediated cross coupling of the bis(thiomethyl)-dithiolethione half with the dithiolone-dicarboxylate half, followed by the double decarboxylation of the TTF-diester [14]. The spectroscopic data of the compound were in agreement with those described in the literature [15]. In the course of our investigations we have succeeded to crystallize this precursor, for which the solid-state structure was unknown. Large size orange single crystals of (MeS)$_2$TTF were grown after several hours from a solution of (MeS)$_2$TTF, in a small volume of diethyl ether, poured in a large excess of hexane. The compound crystallizes in the orthorhombic system, non-centrosymmetric space group $P2_12_12_1$, with one independent molecule in the unit cell (Fig. 1).

All the bond lengths and angles are in the usual range of neutral TTFs, together with the moderate folding of the dithiole ring adjacent to the thiomethyl substituents, amounting to 15.8° around the S3 $\cdots$ S4 hinge. Interestingly, the thiomethyl substituents arrange in a nonsymmetric manner, with the methyl group defined by C8 located above the TTF mean plane (dihedral angle C8S6C6C5 of 103°), while the other methyl group defined by C7 lies practically in the TTF plane (dihedral angle C7S5C5C6 of 161°). In order to evaluate whether this conformation observed in the solid state corresponds to an equilibrium geometry in the gas phase, we have undertaken theoretical calculations at the DFT level, with the B3LYP hybrid functional [16] and the 6-31(+)G(d) basis set. The geometry optimizations provided two energy minima (checked by frequency calculations which were all positive) corresponding to relative *trans* and *cis* orientations of the thiomethyl substituents with respect to the TTF plane (Fig. 2).

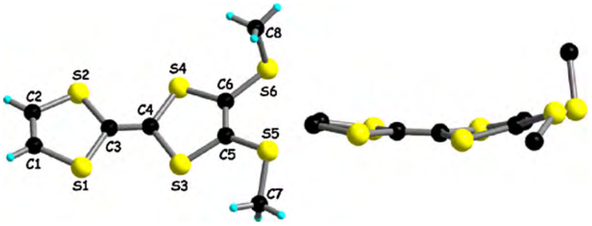


Fig. 1. Molecular structure of (MeS)$_2$TTF (a) and side view of the molecule (b).

The two minima are isoenergetic ($\Delta E_{trans\text{-}cis}$ = 0.39 kcal mole^{-1}) and are characterized by the folding of the dithiole ring adjacent to the substituents, as observed in the experimental solid-state structure. Nevertheless, the orientation of the thiomethyl substituents in both equilibrium conformations is different with respect to the experimental one, since in the *trans* geometry the methyl groups are located above and below the TTF plane

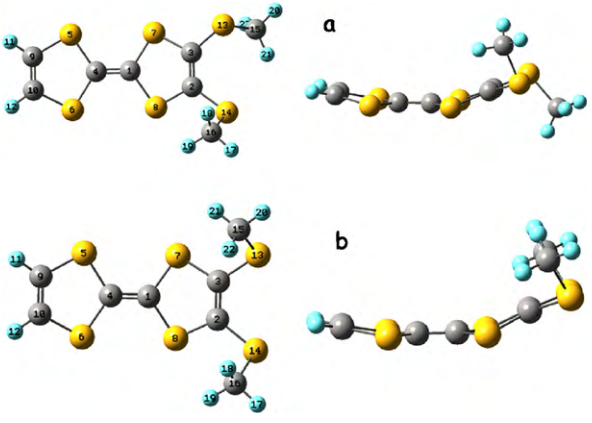


Fig. 2. Optimized geometries for (MeS)$_2$TTF: *trans* (a) and *cis* (b); DFT/B3LYP/6-31(+)G(d).