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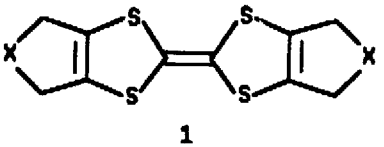
BIS(THIODIMETHYLENE)-TETRATHIAFULVALENE (BTDM-TTF).[1] A NEW π-ELECTRON DONOR WITH RELEVANT OXIDATION PROPERTIES.

C. Rovira*, N. Santaló, J. Veciana.
Centro de Investigación y Desarrollo (C.S.I.C.), Jordi Girona 18-26,
08034 Barcelona, Spain.

Abstract: *The synthesis and some physical properties of a new thioalkyl substituted tetrathiafulvalene, bis(thiodimethylene)tetrathiafulvalene, are reported. Oxidation potentials of BTDM-TTF indicate a low intramolecular Coulomb repulsion energy.*

Since the discovery of low dimensional organic metals based on tetrathiafulvalene (TTF), many structurally related derivatives of TTF have been studied intensively in the last 15 years. Such an enormous amount of research has been motivated by the impressive variety of electrical behaviors (insulators, anisotropic metals and superconductors) showed by the salts derived from this class of one-electron donors[2]. Three general approaches are been used in order to improve the electronic properties of the heterofulvalene π system of TTF (reduce the on-site Coulomb repulsions) and simultaneously to increase the conduction band width and dimensionality of their conducting complex salts: a) Replacement of S with the larger and more polarizable Se and Te atoms[3,4], b) Extension of the π system of TTF by incorporating chalcogen atoms in place of its H atoms[5,6], and c) Extension of the π system by heteroaromatic annelation of TTF.[7]

Replacement of the external methylene groups of hexamethylenetetrathiafulvalene, HMTTF, <u>1a</u> with different heteroatoms could be another alternative way to modify the electronic properties of the heterofulvalenic π system. The foreseeable different strain existing in the external five-membered rings of HMTTF analogues <u>1</u> is expected to perturb differently the heterofulvalenic framework of the neutral donors. Such effect could be of minor importance in the radical cations derived from <u>1</u>, owing to their aromatic character. In addition to this structural tuning of the electronic properties of the donors, the added heteroatoms could give rise to interchain interactions suppressing the various instabilities which often lead to insulating ground states in quasi-one-dimensional organic conductors.

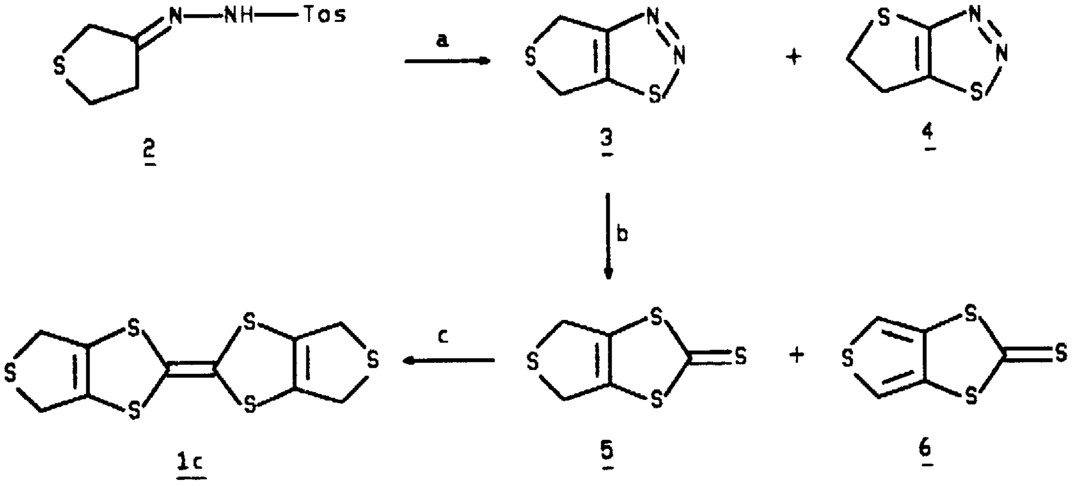


<u>1</u>

<u>1a</u> X= CH_2; **HMTTF**
<u>1b</u> X= O ; **BODM-TTF**
<u>1c</u> X= S ; **BTDM-TTF**
<u>1d</u> X= Se ; **BSDM-TTF**
<u>1e</u> X= SO_2; **BDOTDM-TTF**

We report here the synthesis of a new member of this series[8], bis(thiodimethylene)-tetrathiafulvalene, BTDM-TTF, 1c. Some preliminary results concerning with the oxidation potentials (cyclic voltammetry,CV) and spin distributions (electron spin resonance, ESR) in its cation radical are also described.

BTDM-TTF was synthesized from the tosylhydrazone 2 in a three-steps procedure involving thermal descomposition of 1,2,3- thiadiazole in the presence of carbon disulfide (Scheme 1). The ring closure of tosylhydrazone 2 promoted by thionyl chloride[9] gives a mixture of the two 1,2,3-thiadiazole isomers 3 and 4 in a ca. 1:3 proportion. 4,6-dihydro-[3,4-d]-thieno-1,2,3-thiadiazole (3) and 4,5-dihydro-[2,3-d]-thieno-1,2,3-thiadiazole (4) were separated by means of flash chromatography and identified to be each other by ^{1}H NMR.[10]. Thermolysis of thiadiazole 3 in excess of carbon disulfide (6 h, 170·C) affords the yellow 4,6-dihydro-[3,4-d]-thieno-1,3-dithiole-2-thione (5) as the major product, as well as smaller amounts of the dehydrogenation product thieno-[3,4-d]-1,3-dithiole-2-thione (6).[11]. Direct coupling of thione 5 with excess of trimethyl phosphite (1 h, 120·C) gives bis(thiodimethylene)-tetrathiafulvalene (1c) as a brown microcrystalline powder in 40 % yield, m.p. 222-3º; i.r. (KBr) 2900 m, 2830 m, 1440 w, 1230 w, 1130 m, 1100 w, 1060 m, 875 w, 760 s, 705 s, 630 w, 440 s cm^{-1}; ^{1}H n.m.r. (DMSO-d$_6$) 3,79 (s); u.v-vis (CHCl$_2$CH$_2$Cl) λ(logε) 530 (sh 2,33), 463 (2,56), 365 (sh 3,31), 308 (4,11); m.s. (IE) m/e, 320 (M$^+$, 88).



Scheme 1. Reagents: a, SOCl$_2$ (40 %); b, CS$_2$, 170º, 6 h (62 %); c, (MeO)$_3$P, 120º (40 %).

The electrochemical data, obtained by cyclic voltametry, of several members of series 1 are given in Table 1. BTDM-TTF, as expected, shows two reversible one-electron oxidations with potentials in a suitable range to form organic metals. However, the most remarkable electrochemical result is the low value for the difference between ionization potentials ($\Delta E_{1/2}$= 0.17V), one of the lowest among the known TTF derivatives observed so far. Since this value is a measure of the intramolecular Coulomb repulsion energy, this result suggests that BDTM-TTF is one of the better donors in this respect.

Oxidation of BDTM-TTF with $AlCl_3$ in CH_2Cl_2 gives the corresponding cation-radical. The isotropic ESR spectra shows nine central intense lines due to the coupling with eight equivalent (in the esr-time scale) methylenic protons. Coupling with one isotopic sulfur atom, ^{33}S (I=3/2), at natural abundance is observed upon amplification of the signal as weak structurated satellite lines. The ^{33}S hyperfine coupling constants (hcc) and g-value (Table 1) indicate that spin density distribution on the heterofulvalenic π system of BTDM-TTF$^{+\cdot}$ is very close to those of the other members of the series (and TTF). The differences observed in hcc's of methylenic protons ($a_{^1H(\beta)}$, Table 1) are related with the distinct conformations (and $\cos^2\Theta$ dependence of $a_{^1H(\beta)}$) of the external five-membered rings in each members of the series 1.

TABLE 1 Cyclic Voltammetry[a] and ESR[b] Data

compd.	$^1E^{rev}_{1/2}$	$^2E^{rev}_{1/2}$	$\Delta E_{1/2}$	g_{iso}	$a_{^{33}S}$	$a_{^1H(\beta)}$
TTF	0.39	0.62	0.24	2.0081	0.425	0.125
HMTTF[c]	0.27	0.60	0.33	2.0078	0.420	0.211
BODM-TTF[d]	0.35	0.66	0.31	-	-	-
BTDM-TTF	0.55	0.72	0.17	2.0079	0.425	0.130
BDOTDM-TTF[e]	0.65	0.80	0.15	2.0077	0.425	0.158

a In Volts; DMF/0.1 $TBAPF_6$, r.t., Pt buttom (working) and Pt wire (auxiliary) electrodes, scan rate 200 mV s^{-1}, SCE ref. electrode
b Coupling constants (in mT) of BTDM-TTF are determinated by computer simulation. The other hcc's are from Ref. 12.
c Oxidation potentials measured in CH_3CN/0.1 M $TEAClO_4$. Ref. 13.
d Ref. 8b
e Ref. 14

Electrochemical and ESR results bear out our initial expectation concerning with the structural tuning of the electronic properties of π electron donors.

Further studies to improve the yields and grow ion-radical salts and charge-transfer complexes of BTDM-TTF are in progress.

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