From: ORGANIC AND INORGANIC LOW-DIMENSIONAL
CRYSTALLINE MATERIALS
Edited by Pierre Delhaes and Marc Drillon
(Plenum Publishing Corporation, 1987)

PYRIDINO-TETRAHETEROFULVALENES AND A FEW OF THEIR SALTS

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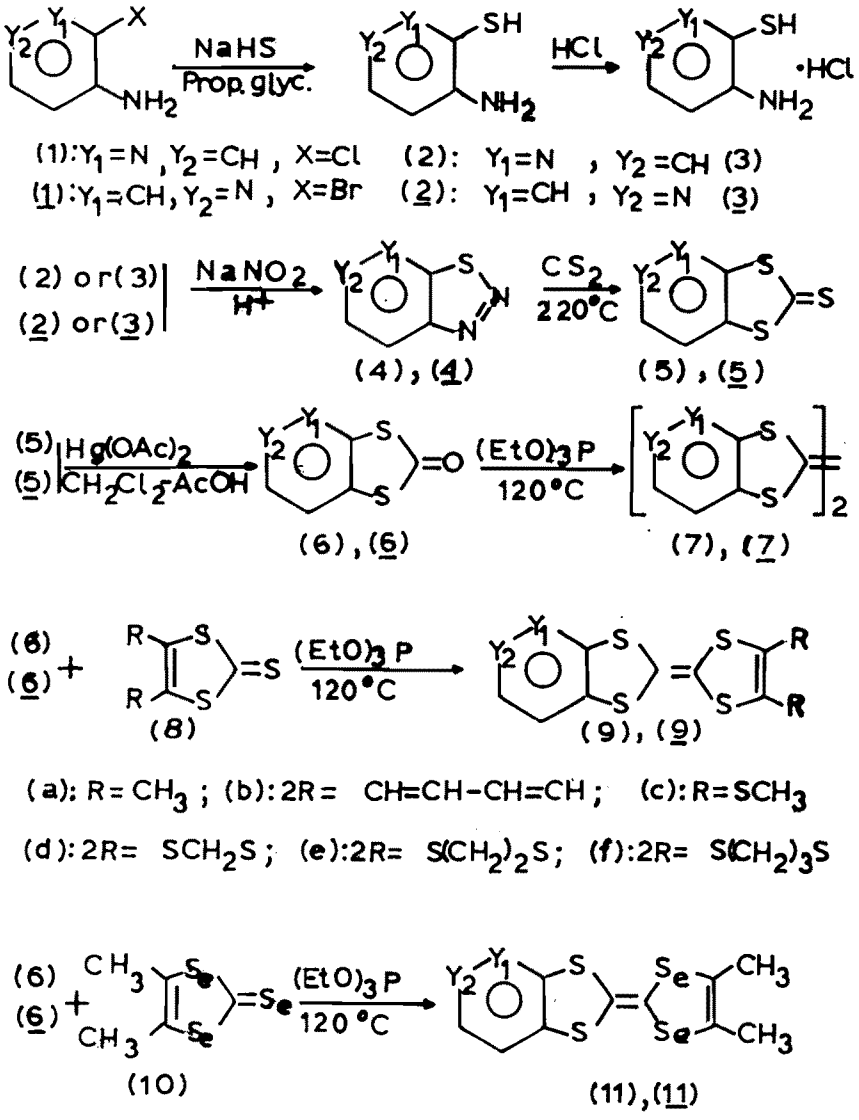
INTRODUCTION

Recently, the unsymmetrical π-donor DMET (dimethylethylenedithio-dithiadiselenafulvalene) has attracted much interest since the discovery of superconductivity in the cation radical salt $(DMET)_2Au(CN)_2$ [1]. In this paper we report the preparation of some new unsymmetrical tetraheterofulvalenes having a pyridino-ring and a few of their salts.

EXPERIMENTAL

The new π-donors (9) and (11) were prepared by cross coupling of 1,3-pyridino[4,5-b]-dithiole-2-one [2]-[4]* and 4,5-dimethyl-1,3-dithiole-2-thione [5], 1,3-benzodithiole-2-thione [6], 4,5-bis(alkylthio)-1,3-dithiole-2-thiones [7] and 4,5-dimethyl-1,3-diselenole-2-selone [8], via triethyl phosphite, $(EtO)_3P$, according to the Scheme 1.** 3-amino-2-chloropyridine (1)[3]*** was used as starting material. The preparation of (9) and (11) by using 4-amino-3-bromopyridine [4],[9] as starting material was unsuccessful because of the low yield of the intermediate products [4]. The preparation of these donors by an alternative method starting from 4-nitro-3-bromopyridine is in progress [4]. Some charge transfer complexes and some cation radical salts were prepared by direct reaction (DR) of the π-donors (9) and (11) with TCNQ, Br_2 and Bu_4NI_3 in CH_2Cl_2. Also some cation radical salts were prepared by electrocrystallization (EL) of some π-donors in presence of Bu_4NX (where $X=I_3$, IBr_2 etc) in CH_2Cl_2. Preparative data are given in Table 1. Electrical conductivity measurements were performed with a four-probe method. Samples were mounted with four fine gold wires and electrical conductivity measurements were supplied by a Keithley Model 220 programmable current source; voltage was measured on a Keithley Model 602 electrometer.

*Compound (6) is a white solid, mp=110°C [4].
**Compound (7) was obtained as a yellow solid, mp>300°C [4].
***Commercial (1) was used without further purification.



Scheme 1

RESULTS AND DISCUSSION

Conductivity measurements on polycrystalline compactions of (9b)TCNQ, β-(9e)$_x$Br$_3$ and (11)TCNQ showed that the compounds are neutral complexes similar to (DBTTF)TCNQ [10]. All the rest salts of the Table 1 were found to be conductive. Conductivity measurements on single crystals of α-(9e)$_2$IBr$_2$ along the needle axis (which is the a-axis [11])showed a semiconducting behaviour [12] with activation energy 230meV and σ_{RT}= 3 - 7x10^{-3} Ω^{-1}cm^{-1}. Conductivity measurements on single crystals of the new salts are now underway.

ACKNOWLEDGEMENT

We would like to thank Dr.D.Rigas and Prof.N.Alexandrou for recording mass spectra and Dr.E.I.Kamitsos and M.A.Karakassides for optical and electrical measurements.

Table 1. Preparative data

Compound	Method	Yield(%)	Appearance	mp/°C	UV(λ/nm)+
(9a)		9	yellow	199	390
(9b)		4	yellow	248	350
(9c)		7	orange-yellow	117	358
(9d)		6	yellow	206	450
(9e)		10	orange-yellow	238	358
(9f)		3	yellow	208	354
(11)		15	orange	217	360
(9a)TCNQ*	DR		black powder		
β-$(9a)_xI_3$	DR		small black needles		
(9b)TCNQ*	DR		small brown needles		
β-$(9d)_xI_3$	DR		small black-golden needles		
$(9e)_x$TCNQ	DR		small black needles		
α-$(9e)_xBr_3$	EL		small black - bronze crystals		
β-$(9e)_xBr_3$	DR		brown needles		
α-$(9e)_xI_3$	EL		bronze needles or plates		
β-$(9e)_xI_3$	DR		brown-bronze powder		
α-$(9e)_2IBr_2$**	EL		black needles		
$(11)_x$TCNQ	DR		small orange--brown plates		
α-$(11)_xI_3$++	EL		bronze needles		
α'-$(11)_xI_3$++	EL		bronze-golden spears		
β-$(11)_xI_3$	DR		small black--bronze needles		
α-$(11)_xIBr_2$	EL		small black needles or plates		
β-$(11)_xIBr_2$	DR		black powder		
α-$(11)_x \cdot PF_6$	EL		black needles		

+ Peak position of the longest wavelength band (CH_3CN)

* From elemental analysis

**From x-ray crystal structure solution

++The resonance Raman spectra of both salts (α-,α'-) showed bands at 107, 214, 320...cm^{-1}, which are characteristic of I_3 (linear, symmetric).

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