

# NOTE

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## BIS[4,5-b]PYRIDINO-1,1',3,3'-TETRATHIAFULVALENE: SYNTHESIS AND CHARGE TRANSFER COMPLEXES

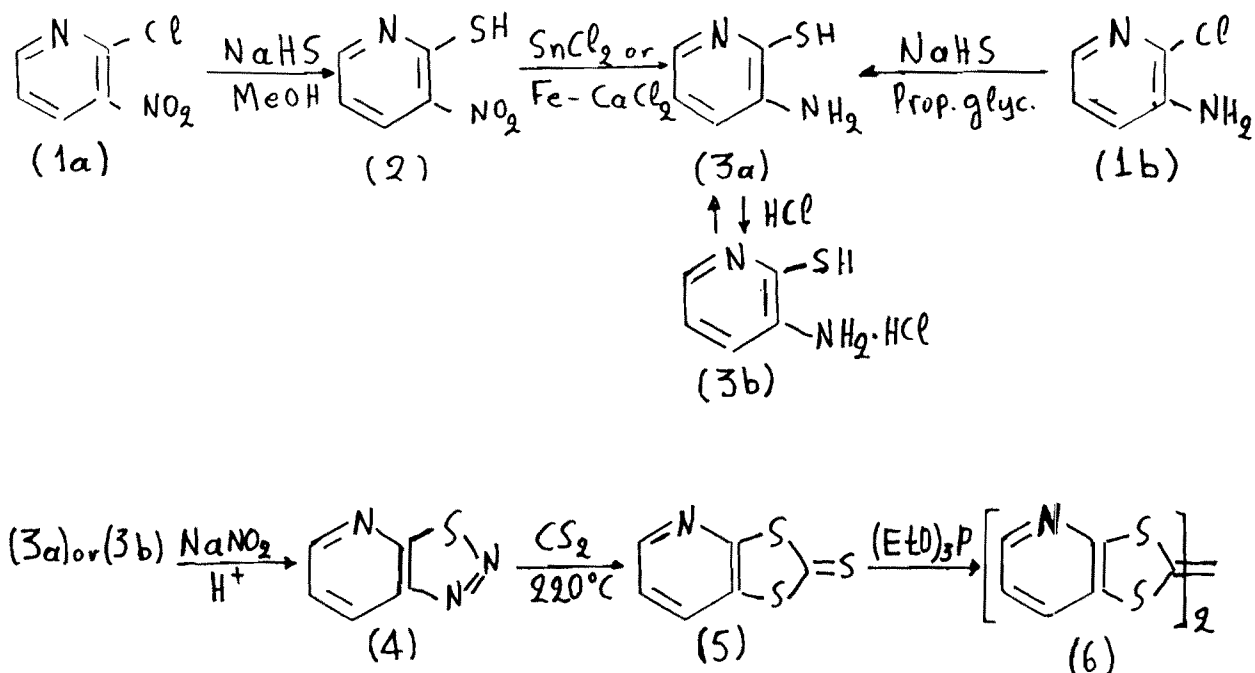
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### Introduction

The interest in solid state properties of the simple salts of organic sulfur or selenium containing  $\pi$ -donors was increased last years because of the observation of ambient pressure superconductivity in the salts  $(\text{TMTSF})_2\text{ClO}_4$  and  $(\text{BEDTTF})_2\text{I}_3$  [where TMTSF=tetramethyltetraselenafulvalene and BEDTTF = bis (ethylenedithio) tetrathiafulvalene]<sup>1-3</sup>. In this paper the preparation of bis [4,5-b] pyridino--1,1',3,3'-tetrathiafulvalene (abbreviated as B[4,5-b] PTF), of a number of its charge transfer complexes and preliminary results of their electrical and optical properties are described. The new  $\pi$ -donor was prepared according to the scheme 1.



Scheme 1

2-Chloro-3-nitropyridine (1a) was transformed to 2-mercapto-3-nitropyridine (2)<sup>4</sup>. 2-Chloro-3-aminopyridine (1b)<sup>5,6</sup> or compound (2)<sup>4,7</sup> was transformed to 2-mercapto-

3-aminopyridine (3a)\*. Compound (3a) or its hydrochloric salt (3b)<sup>5</sup> was transformed to 1,2,3-pyrido-[4,5-b] thiadiazole (4)<sup>7,8</sup>. Reaction of thiadiazole (4) in carbon disulfide at 220°C in an autoclave afforded 1,3-pyrido [4,5-b] dithiol-2-thione(5)<sup>7</sup>. Refluxion of a solution of (5) in triethylphosphite afforded B[4,5-b] PTTF (6). By electrooxidation of a CH<sub>2</sub>Cl<sub>2</sub>-solution of (6) in presence of Bu<sub>4</sub>N<sup>+</sup>X<sup>-</sup> (where X<sup>-</sup> = BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, Br<sup>-</sup>, I<sub>3</sub><sup>-</sup> etc) a number of charge transfer complexes was obtained.

## Experimental

### Materials and instrumentation

Commercial 2-chloro-3-nitropyridine and 2-chloro-3-aminopyridine were used as starting materials without further purification. Also, commercial triethylphosphite was used after double distillation. Elemental analysis was performed by ILSE BEETZ mikroan. Lab., 8640 Kronach (W. Germany). Conductivity measurements were made by the four probe-method using a Keithley-225 current source, a Keithley-614 electrometer (μA), and a Keithley-602 electrometer (mV). The reflectance and absorption spectra were recorded on a Varian -2390 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Varian FT 80A NMR spectrophotometer.

### Preparation of bis[4,5-b]pyridino-1,1'3,3'-tetrathiafulvalene.

2g of 1,3-pyrido[4,5-b]dithiol-2-thione (5) were dissolved in 8ml of warm triethylphosphite and the resulting solution was heated at reflux temperature for 10min. The solution was cooled and the resulting «first» precipitate was filtered, washed with ethanol and dried (yield: 18-25%). The compound was found to be soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>CN etc. Recrystallization from CHCl<sub>3</sub> gave a golden yellow solid (mp=278°C). M.Calc. 306.5, found (mass spectroscopy) 306.

Analysis (%):

for C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>S<sub>4</sub>(306.5); Calcd:C, 47.03;H, 1.97;N,9.15;S,41.85; Found: C, 47.16; H,2.13;N,9.17;S,41.92; UV(CH<sub>3</sub>CN); λ/nm(ε)358: (2290), 302(3420), 280(3420), 211(8700); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.23, 8.17, 7.44, 7.42, 7.30, 7.23, 7.09, 7.02. A very small amount of a «second» precipitate was obtained after cooling the filtrate at -15° C. UV (CH<sub>3</sub>CN); λ/nm(ε)\*\* :330(2400), 302(3310), 278(3200), 212(8700). It was suggested that the «first» precipitate is the thermodynamically more stable transform of (6) (t-B[4,5-b] PTTF) and the «second» precipitate the cis-form c-B[4,5-b]PTTF).

### Preparation of the charge transfer complexes

Charge transfer complexes of the type (B[4,5-b]PTTF)<sub>n</sub>X were prepared by the electrocrystallization of t-B[4,5-b] PTTF (1.55×10<sup>-3</sup>M) and Bu<sub>4</sub>N<sup>+</sup>X<sup>-</sup> (5×10<sup>-3</sup>M, where X=BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, Br, I<sub>3</sub> etc) in CH<sub>2</sub>Cl<sub>2</sub> using platinum electrode at

\* Also Se-analogs of (3)-(5) were prepared by similar methods using NaHSe and CSe<sub>2</sub> instead of NaHS and CS<sub>2</sub>, respectively.<sup>8</sup>

\*\* ε-value of 212nm of the «second» precipitate was considered to be equal to that of 211nm of the «first» precipitate.

1  $\mu\text{A}/\text{cm}^2$  at 22°C. The length of the anodic oxidation was varied allowing for 35% and 10% oxidation of the neutral B[4,5-b] PTF. The 35% oxidation required 2-3 days while the 10% oxidation was completed in 2 days. This short term oxidation was carried out so that the earliest formed crystals could be used. The crystals were washed with  $\text{CH}_2\text{Cl}_2$  and air dried.  $(\text{B}[4,5\text{-b}]\text{PTTF})_2\text{BF}_4$  which was the extensively studied compound is crystallized in copper-black needles with lustrous appearance.

Analysis:

for  $\text{C}_{24}\text{H}_{12}\text{N}_4\text{S}_8\text{BF}_4$  (699.77); Calcd: C, 41.19; H, 1.72; N, 8.02; S, 36.66; Found: C, 41.15; H, 2.14; N, 8.00; S, 36.33. Also the compounds with  $\text{X}=\text{ClO}_4$ ,  $\text{PF}_6$ ,  $\text{Br}_3$ ,  $\text{I}_3$  etc were obtained in crystalline forms.

### Electrical and Optical Properties and Discussion

The dc-conductivity of compressed pellets of  $(\text{B}[4,5\text{-b}]\text{PTTF})_n\text{X}$  measured at room temperature ( $\sigma_{\text{RT}}$ ) was found to be of the order of  $10^{-1}\Omega^{-1}\text{cm}^{-1}$ , namely higher than that of  $(\text{BPTTF})_n\text{X}$  [where BPTTF is bis (pyrazino) tetrathiafulvalene]<sup>9-12</sup> and of the same order of magnitude as that of  $(\text{DBTTF})_n\text{X}$  and Se analogs (where DBTTF=dibenzo-tetrathiafulvalene)<sup>13,14</sup>. Also were found similarities in the reflectance and absorption spectra. The reflectance spectrum of a compressed pellet of  $(\text{B}[4,5\text{-b}]\text{PTTF})_2\text{BF}_4$  for example, is similar to that of  $(\text{BPTTF})_2\text{BF}_4$ <sup>11</sup>; it shows bands at 235,300 (sh), 380-430, 490 (sh), 630,900 (sh) and an upward slope from 1500 nm to longer wavelengths. The value of the reflectivity at 2500 nm was found to be 0.16, while that of  $(\text{BPTTF})_2\text{BF}_4$  ( $\sigma_{\text{RT}}=10^{-2}\Omega^{-1}\text{cm}^{-1}$ )<sup>11</sup> and  $(\text{DBTTF})_8(\text{SnCl}_6)_3$  ( $\sigma_{\text{RT}}=100\Omega^{-1}\text{cm}^{-1}$ )<sup>15</sup> was 0.14 and 0.76, respectively.

The absorption spectrum of  $(\text{B}[4,5\text{-b}]\text{PTTF})_2\text{BF}_4$  rubbed on a quartz plate shows the same bands as those of the reflectance spectrum. The electrical and optical data obtained from  $(\text{B}[4,5\text{-b}]\text{PTTF})_2\text{BF}_4$  indicate that the new donor and selenium analogs could be used for preparation materials with conductivity higher than that of  $(\text{BPTTF})_n\text{X}$ . Detail studies on a large number complexes of B[4,5-b]PTTF and selenium analogs will be subject of a future paper.

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### Summary

Bis [4,5-b] pyridino-1,1',3,3'-tetrathiafulvalene was prepared as a golden-yellow solid after refluxing of a solution of 1,3-dithiole [4,5-b] pyridine-2-thione [RN:69212-30-2] in neat triethylphosphite and cooling. Electrooxidation of its  $\text{CH}_2\text{Cl}_2$ -solutions in presence of  $\text{Bu}_4\text{N}^+\text{X}^-$  (where  $\text{X}^- = \text{BF}_4$ ,  $\text{ClO}_4$ ,  $\text{PF}_6$ ,  $\text{Br}^-$ ,  $\text{I}_3^-$  etc) gave conducting and highly reflecting crystalline solids.

**Key words:** Tetrathiafulvalenes,  $\pi$ -donors, charge transfer complexes, synthetic metals.

### Περίληψη

*Δι[4,5-b] πυριδίνιο-1,1',3,3'-τετραθειαφουλβαλένιο: Σύνθεση και σύμπλοκα μεταφοράς φορτίου.*

Το δι[4,5-b] πυριδίνο-1,1',3,3'-τετραθειαφουλβαλένιο παρασκευάστηκε σαν χρυσοκίτρινο στερεό μετά από βράσιμο σε φυάλη με κατακόρυφο ψυκτήρα διαλύματος 1,3-διθειολο-[4,5-b] πυριδίνο-2-θειόνης [RN:69212-30-2] σε φωσφορώδη τριαιθυλεστέρα. Ηλεκτροοξείδωση διαλυμάτων αυτού σε  $\text{CH}_2\text{Cl}_2$  παρουσία  $\text{Bu}_4\text{N}^+\text{X}^-$  (όπου  $\text{X}^- = \text{BF}_4^-, \text{ClO}_4^-, \text{PF}_6^-, \text{Br}^-, \text{I}_3^-$  etc) έδωσε αγωγιμα κρυσταλλικά υλικά με λάμπουσα επιφάνεια.

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