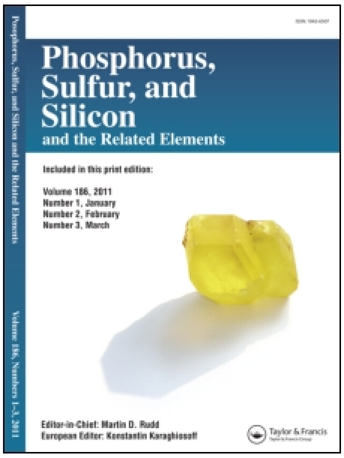


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF CHARGE-TRANSFER COMPLEXES CONTAINING A NOVEL *BIS*-SUBSTITUTED BENZO[B]THIOPHENE TTF DONOR MOLECULE

Peter D. Clark[a]; A. S. Hinman[a]; Shaun T. E. Mesher[a]
[a] Department of Chemistry, The University of Calgary, Alberta, Canada

To cite this Article Clark, Peter D. , Hinman, A. S. and Mesher, Shaun T. E.(2000) 'SYNTHESIS OF CHARGE-TRANSFER COMPLEXES CONTAINING A NOVEL *BIS*-SUBSTITUTED BENZO[B]THIOPHENE TTF DONOR MOLECULE', Phosphorus, Sulfur, and Silicon and the Related Elements, 164: 1, 153 — 159

To link to this Article: DOI: 10.1080/10426500008045241

URL: http://dx.doi.org/10.1080/10426500008045241

Phosphorus, Sulfur and Silicon, 2000, Vol. 164, pp. 153-159
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF CHARGE-TRANSFER COMPLEXES CONTAINING A NOVEL *BIS*-SUBSTITUTED BENZO[*B*]THIOPHENE TTF DONOR MOLECULE

PETER D. CLARK*, A.S. HINMAN and SHAUN T.E. MESHER

Department of Chemistry, The University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada, T2N 1N4

(Received December 17, 1999; In final form March 29, 2000)

Benzo[*b*]thiophene was successfully converted to 2-(benzo[*b*]thieno[2,3-*d*]-1,3-dithiol-2-ylidene)-benzo[*b*]thieno[2,3-*d*]-1,3-dithiole (BT-TTF). Charge transfer complexes of BT-TTF with TCNQ, I_3 and $SbCl_6$ were synthesised and their conductivities 0.4, 0.12 and 0.024 σ/scm^{-1} respectively, were measured as compressed power pellets.

Keywords: Benzo[*b*]thiophene; tetrathiafulvalene derivative

INTRODUCTION

The synthesis of new donor molecules for the construction of organic based conductors is a rapidly growling and exciting area of research[1]. The building blocks of many of these conductors are derivatives of tetrathiafulvalene (TTF) and their Se and Te analogues. Many of the new donor molecules reported in the literature incorporating a TTF unit focus on modifications to the TTF unit by the addition of one or more side chains[2]. Changes to the central carbon-carbon double bond have also been investigated. By adding an electron rich spacer, elongated π-systems have been synthesised[3]. Highly aromatic systems such as perylene can also act as excellent donor molecules and a number of aromatic heterocyclic systems such as 1,7-dithiaperylene have also been investigated[1].

---

* Corresponding author.

With this understanding, we decided to synthesise a polycyclic donor molecule comprised of benzo[*b*]thiophene (**1**) and TTF. Herein we report the successful synthesis of 2-(benzo[*b*]thieno[2,3-*d*]-1,3-dithiol-2-ylidene)-benzo[*b*]thieno-[2,3-*d*]-1,3-dithiole (BT-TTF) (**6**) an elongated π-system donor molecule. The preparation of conducting complexes of **6** with TCNQ, I_2 and $Bu_4N^+SbCl_6^-$ is reported along with the electrochemical properties of **6**.

BT-TTF (**6**) was synthesised by reaction of **1** with dimethyl disulfide in the presence of clayzic[4] to afford 2,3-*bis*(methylthio)benzo[*b*]thiophene **2** (74%)[5]. Reduction of **2** was achieved with sodium metal and ammonia[6] to give the dithiol **3** (88%). To avoid oxidation to the disulfide, crude product **3** was mixed directly with thiophosgene[7] to afford benzo[*b*]thieno[2,3-*d*]-1,3-dithiol-2-thione (**4**) (65%). The structure of this compound was confirmed by x-ray analysis[8] as complete characterization of **3** proved difficult. Cross-coupling of **4** with triethyl phosphite failed to yield **6**, subsequently, the thione was oxidised with $KMnO_4/PhCO_2H$ under phase transfer conditions[8] to furnish benzo[*b*]thieno[2,3-*d*]-1,3-dithiol-2-one (**5**) (63%). The ketone **5** was then heated to 160°C in triethyl phosphite to yield **6** (38%). HPLC (hexane/THF) analysis of **6** indicated the presence of two compounds in equal proportion. Mass spectra and ^1H NMR spectra suggested these compounds were the Z- and E- isomers (**6a + b**).

The cyclic voltammetry of (**6a + b**) in methylene chloride showed two reversible one-electron oxidations, with half-wave potentials of 0.540V and 0.995V vs SCE (see Figure 1).

The charge-transfer (CT) complexes were synthesised by the addition of equimolar quantities of TCNQ, I_2 or $Bu_4N^+SbCl_6^-$ to a solution of **6** in CS_2[10]to afford **7, 8** and **9**. In each case, a highly insoluble black solid precipitated out of solution. Elemental analyses of **7, 8** and **9** indicated donor/acceptor ratios of 1:1, although with the insoluble nature of these salts made purification and recrystallisation very difficult. Electrocrystallisation of **6** with $Bu_4N^+PF_6^-$, has to date, failed to yield a single crystal, probably as a result of low solubility of **6** in organic solvents. The conductivities (see Table I) of compressed pellets formed from each CT complex were measured via a four probe technique at room temperature. These data show that conductivities decrease as the counter anion became less linear in structure.

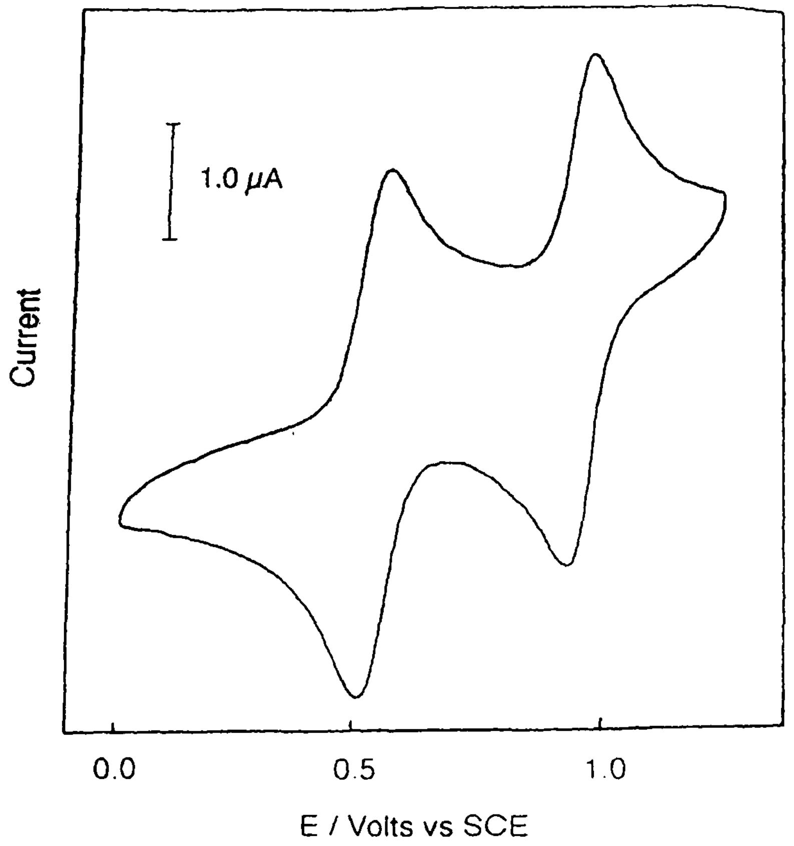


FIGURE 1 Cyclic Voltammetry of 6, in CH_2Cl_2/Bu_4NPF_6 (0.1 M); Scan Rate 100 mV/s at **Room Temperature**

TABLE I Conductivity of the CT Complexes

CT Complex	*δ/scm^{-1}*
BT-TFF•TCNQ	0.12
BT-TFF•I_3	0.4
BT-TTF•$SbCl_6$	0.024

At present, we are investigating the synthesis of derivatives of **6** with the goal of producing more soluble compounds and elongating the π-system.

We gratefully acknowledge Alberta Sulphur Research Ltd. for financial support of this research.

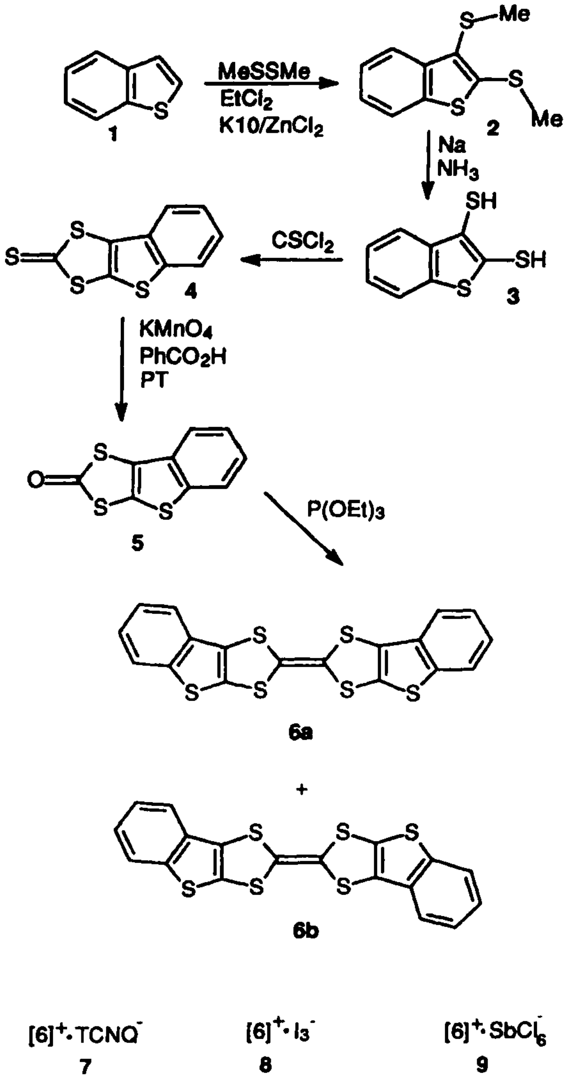
EXPERIMENTAL

Organic chemicals were obtained from commercial suppliers and were used without purification. Solvents were dried and purified according to standard procedures. NMR spectra were recorded on a Bruker AMX2 – 300 or AM400 spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (ppm) internally referred to TMS. Mass spectra were obtained on a Hewlett Packard HP5890. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were obtained by D. Fox on a Control Equipment Corporation 440 EA, in the Analytical Services Laboratories of the Department of Chemistry at The University of Calgary.

Preparation of (4)

Under a nitrogen atmosphere, sodium metal (2.02 g, 88 mmol) was added to a solution of 2,3-*bis*(methylthio)benzo[*b*]thiophene **1** (5.00 g, 22 mmol) and liquid ammonia (300 mL). After 14h, the reaction was quenched with a saturated solution of NH_4Cl (aqueous, 50 mL). The aqueous layer was washed with ether (30 mL × 2) and then was acidified with 6M HCl. The acidic layer was extracted with dichloromethane (3 × 25 mL), the organic layer was then dried, filtered and evaporated to afford a yellow oil, benzo[*b*]thiophene-2,3-dithiol **3** (3.83 g, 88%).

The crude dithiol **3** (3.83 g, 19.3 mmol), triethylamine (5.4 mL, 38.6 mmol), and dichloromethane (250 mL) were mixed together at 0–5°C. A solution of thiophosgene (2.66 g, 23 mmol) in dichloromethane (50 mL) was added dropwise to the mixture which was then allowed to warm up to room temperature. The reaction mixture was stirred overnight and was evaporated under reduced pressure to yield a brown solid. The solid was redissolved in carbon disulfide (100 mL) and washed with 2M HCl (50 mL), saturated aqueous $NaCO_3$ (50 mL), and water (50 mL). The solution was then dried ($MgSO_4$), filtered and evaporated to afford a brown solid. The solid was recrystallisied from benzene with cooling



SCHEME 1

(0°C). The solid benzene mixture was then placed in a filter funnel and washed with cold hexane (until no benzene remains) to afford benzo[*b*]thiophene[2,3-*d*]-1,3-dithiole-2-thione **4** as yellow crystals (3.01 g, 65%), mp

143–144°C. (Found C, 44.85; H, 1.57. $C_9H_4S_4$ requires C, 44.97; H, 1.68%); δ_H (300 MHz) 7.88 (1H, m), 7.59 (1H, m) and 7.50–7.40 (2H, m); δ_C (75 MHz) 213.3 (q), 142.1 (q), 133.3 (q), 133.0 (q), 131.8 (q), 125.8 (q), 125.8 (CH), 125.4 (CH), 123.3 (CH) and 121.7 (CH); m/z 240 (M^+, 100%).

Preparation of (5)

A mixture of potassium permanganate (2.47 g, 15.6 mmol), benzo[*b*]thiophene[2,3-*d*]-1,3-dithiole-2-thione **4** (1.25 g, 5.2 mmol), benzoic acid (0.64 g, 5.2 mmol), and tetraethylammonium chloride (0.19 g, 1.0 mmol) was stirred vigorously in the presence of water (250 mL) and dichloromethane (125 mL) for 24 h. Aqueous, concentrated sodium metabisulfite was added until the mixture attained a beige color. The resultant mixture was filtered through a celite pad and the organic layer was washed with 1M aqueous hydrazine hydrochloride (40 mL), saturated sodium carbonate solution (40 mL) and with a saturated brine solution (40 mL). The organic layer was dried ($MgSO_4$), filtered and evaporated to afford a yellow solid benzo[*b*]thieno[2,3-*d*]-1,3-dithiole-2-one **5**as yellow powder (0.77 g, 65%), mp 98–99°C. (Found C, 47.78; H, 1.63. $C_9H_4OS_3$ requires C, 48.19; H, 1.80%); δ_H (400 MHz) 7.82 (1H, d, J=7.7 Hz), 7.48 (1H, d, J=7.4 Hz) and 7.42–7.34 (2H, m); δ_C(100 MHz) 192.6 (q), 139.2 (q), 133.1 (q), 125.4 (CH), 124.9 (CH), 123.5 (q), 122.7 (CH), 121.8 (q), and 121.7 (CH); m/z 224 (M^+, 45%).

Preparation of (6)

Benzo[*b*]thieno[2,3-*d*]-1,3-dithiole-2-one **5** (170 mg, 0.8 mmol) was dissolved in triethyl phosphite (2 mL) and the solution was heated to 160°C, (approximately 1 hour). After 1 h, the reaction was cooled and an orange precipitate was collected by filtration. The solid was washed with methanol and dried to yield 2-(benzo[*b*]thieno[2,3-*d*]-1,3-dithiole-2-ylidene)-benzo[*b*]thieno[2,3-*d*]-1,3-dithiole (BT-TTF) **6** as an orange solid (63 mg, 38%), mp 255–257°C. (Found C, 52.07; H, 1.58. $C_{18}H_8S_6$ requires C, 51.89; H, 1.94%); δ_H(400 MHz) 7.76 (2H, d, J=8.2 Hz), 7.45–7.39 (4H, m), 7.34–7.29 (2H, m); δ_C ($CS_2/CDCl_3$, 100 MHz) 142.5 (2q), 132.3 (2q), 128.2 (2q), 126.8 (2q), 125.1 (2CH), 123.9 (2CH), 122.8

(2CH), 121.0 (2CH), and 117.9 (2q); m/z 416 (M^+, 100%); $E_{1/2}$ = 0.540V, $E_{1/2}$= 0.955V vs SCE.

Preparation of BT-TTF-TCNQ (7)

A solution of TCNQ (41 mg, 0.2 mmol) in acetonitrile (100 mL) was added dropwise to a refluxing solution of benzene (50 mL) and BT-TTF **6** (83 mg, 0.2 mmol), in the absence of light and under a nitrogen atmosphere. After 2 h, the reaction was allowed to cool down to room temperature and then the mixture was filtered to remove unreacted BT-TTF **6**. Evaporation of the solvent under reduced pressure afforded a black solid BT-TTF•TCNQ **7** (60 mg, 48%). (Found C, 58.32; H, 2.26. $C_{30}H_{12}N_4S_6$requires C, 58.04; H 1.95%).

Preparation of BT-TTF•I_3 (8) and BT-TTF•$SbCl_6$(9)

Potassium iodide or $Bu_4N^+Sb^-Cl_6^-$ (0.2 mmol) was dissolved in dichloromethane (50 mL) and added dropwise to a stirred solution of BT-TTF **6** (83 mg, 0.2 mmol) in carbon disulfide (50 mL). The addition was done in the dark and at a rate of 5 mL/min. After 10 min, a black precipitate was filtered and dried, to afford **8** (130 mg, 81%), or **9** (50 mg, 33%).

References

[1] J.M. Williams, J.R. Ferraro, R.J. Thron, K.D. Carlson, H. Geiser, H.H. Wang, A.M. Kini and M. Whangbo, Organic Superconductors (including Fullerenes): Synthesis, Structure Properties and Theory (Prentice Hall, NJ, 1992).

[2] A.J. Moore, M.R. Bryce, A.S. Batsanov, J.C. Cole and J.A.K. Howard, *Synthesis*, 675 (1995).

[3] K. Takahashi and K. Tomitanti, *Chem. Soc., Chem. Commun.*, 821 (1995).

[4] J.H. Clark, S.R. Cullen, S.J. Barlow and T.W. Bastock, *J. Chem. Soc. Perkin Tran. 2*, **6**, 1117 (1994).

[5] P.D. Clark, S.T.E. Mesher and A. Primak, *Phosphorus, Sulfur, and Silicon*, **114**, 99–108 (1996).

[6] C.W. Dirk, S.D. Cox, D.E. Wellman and F. Wudl, *J. Org. Chem.*, **50**, 2395 (1985).

[7] R. Bindra, H. Singh, S. Sharma and R.N. Iyer, *Indian J. Pharm.*, **35**, 133 (1975).

[8] M. Parvez, S.T.E. Mesher and P.D. Clark, *Acta Cryst.*, **C52**, 1503–1505 (1996).

[9] R.A. Atkin, D.P. Armstrong and S.T.E. Mesher, *Tet. Lett.*, **35**, 6143 (1994).

[10] M.A. Fox and H-L Pan, *J. Org. Chem.*, **59**, 6519 (1994).