

# The First Synthesis of Bis-Fused 1,10-Phenanthrolines via Double Photocyclization of *N,N*-Disubstituted *o*-Phenylenediamine

Tarek Abou Elmaaty, Lyle W. Castle\*

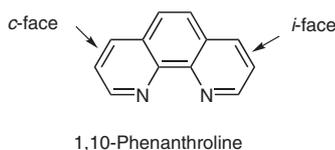
Chemistry Department, Idaho State University, Campus Box 8023, Pocatello, ID 83209, USA  
 Fax +1(208)2824373; E-mail: castlyle@isu.edu

Received 28 November 2005; revised 19 December 2005

**Abstract:** Bis[1]benzothieno[2,3-*c*;3',2'-*i*][1,10]phenanthroline was prepared in four steps starting from *o*-phenylenediamine with a double photocyclization as the key step to construct the 1,10-phenanthroline moiety.

**Key words:** heterocycles, 1,10-phenanthrolines, photocyclization

Chelating agents such as 1,10-phenanthrolines have gained importance as water-splitting agents, molecular switches, and artificial nucleases (DNA cleavers).<sup>1</sup> Research in our laboratory has been centered around the synthesis of new *c*-fused aromatic 1,10-phenanthrolines using a photocyclization reaction to construct the skeleton of the 1,10-phenanthroline moiety.<sup>2</sup> This extends this research area by generating 1,10-phenanthrolines that are fused on both the *c*- and *i*-face (Figure 1).



**Figure 1**

The key reaction involves a double photocyclization that generates the 1,10-moiety in a single step. This method is unique in that it generates a bis-fused 1,10-phenanthroline ring system in one reaction. This method could be used to generate compounds containing two or more 1,10-phenanthroline moieties. Compounds of this nature will be especially useful in the fields of organometallic polymers and molecular switches.

The synthesis of our target compound bis[1]benzothieno[2,3-*c*;3',2'-*i*][1,10]phenanthroline (**6**) is accomplished in four steps from known starting materials. In the first step, *o*-phenylenediamine (**1**) is reacted with 3-chlorobenzo[*b*]thiophene-2-carbonyl chloride (**2**) to form the diamide *N,N'*-(1,2-phenylene)di-3-chlorobenzo[*b*]thiophene-2-carboxamide (**3**) which is photocyclized in DMF to form the bislactam **4**. Reaction of **4** with  $\text{POCl}_3$  generated the dichloro compound **5**, which can be subjected to catalytic hydrogenation to form the target **6** (Scheme 1).

Previously, photocyclization reactions to generate the 1,10-phenanthroline moiety have been carried out in cyclohexane or benzene.<sup>2</sup> Often the use of these solvents would limit the quantity of material that could be reacted (200–500 mg). Due to the extremely low solubility of the amides in this work, we explored the use of DMF as a photocyclization solvent. It was found that using DMF as a solvent allowed for the reaction to be scaled up (tenfold), with excellent yields. Also, when using DMF the lactam is obtained in high purity generating material that can be used directly in the next step. The <sup>1</sup>H NMR spectrum of **6** revealed two singlets at 9.38 and 9.83 ppm corresponding to H-15/16 and H-6/9, respectively. A COSY spectrum shows the expected four spin system corresponding to H-1/14, H-2/13, H-3/12, and H-4/11. The doublet resonating at 9.13 ppm, corresponding to H-1/14 correlates with the multiplet at 7.80 ppm that corresponds to H-2/13 and H-3/12. This multiplet correlates with the doublet resonating at 8.38 ppm corresponding to H-4/11. The <sup>13</sup>C NMR spectrum shows resonances corresponding to the six CH carbons, however, due to the low solubility of **6**, even after an overnight run, none of the quaternary carbon resonances were observed. Finally, HRMS confirmed that the cyclization had occurred.

In conclusion, we have presented the first synthesis of the 1,10-phenanthroline moiety via a double photocyclization reaction. This method should be applicable to the synthesis of other similar systems. This ring system is unique in that it contains two bay regions and is a dipyrrodothieno analogue of the hitherto unknown dibenzo[*a,o*]picene ring system.<sup>3</sup>

All melting points were obtained in open capillary tubes and are uncorrected. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined on a Varian Mercury 300 MHz FT NMR 300 with DMSO-*d*<sub>6</sub> as solvent with chemical shifts reported in ppm relative to TMS as internal standard. Electrospray MS were carried out on a Waters Autospec Ultima Magnetic Sector MS. Microanalysis was performed in house using a Perkin Elmer Series II CHNS/O Analyzer 2400. Reagents were purchased from Aldrich.

## *N,N'*-(1,2-Phenylene)di-3-chlorobenzo[*b*]thiophene-2-carboxamide (**3**)

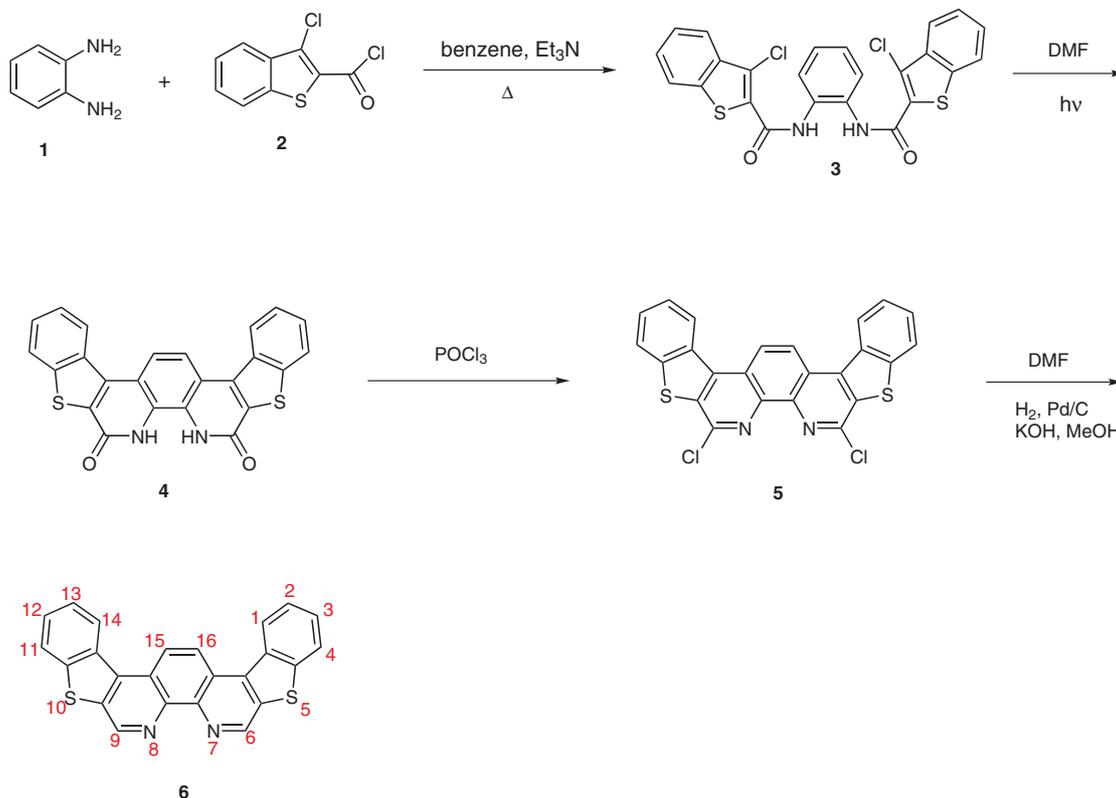
3-Chlorobenzo[*b*]thiophene-2-carbonyl chloride (**1**; 2.3 g, 10 mmol) and *o*-phenylenediamine (**2**; 2.84 g, 20 mmol) were dissolved in benzene (50 mL) and were heated at reflux for 4 h. The reaction mixture was allowed to cool to r.t., then the deposited solid was collected by filtration and crystallized (EtOH) to give colorless crystals; yield: 80%; mp 253 °C.

SYNTHESIS 2006, No. 9, pp 1402–1404

Advanced online publication: 11.04.2006

DOI: 10.1055/s-2006-926441; Art ID: M08005SS

© Georg Thieme Verlag Stuttgart · New York



Scheme 1

$^1\text{H NMR}$  (DMSO- $d_6$ ):  $\delta$  = 7.38 (dd,  $J$  = 6.0, 4.5 Hz, 2 H), 7.62 (m, 4 H), 7.78 (dd,  $J$  = 6.0, 4.5 Hz, 2 H), 7.92 (d,  $J$  = 7.0 Hz, 2 H), 8.18 (d,  $J$  = 7.0 Hz, 2 H), 10.02 (s, 2 H NH).

Anal. Calcd for  $\text{C}_{24}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_2\text{S}_2$ : C, 57.95; H 2.84; N, 5.63. Found: C, 58.02; H 2.74; N, 5.99.

#### Bis[1]benzothieno[2,3-*c*;3',2'-*i*][1,10]phenanthroline-6,9(7*H*,8*H*)dione (4)

A stirred solution of **3** (0.99 g, 2 mmol) was dissolved in DMF (200 mL) and placed in the photocyclization reaction vessel. To this solution was added  $\text{CHCl}_3$  (600 mL) and  $\text{Et}_3\text{N}$  (0.1 mL). The resulting solution was irradiated with a 450-W Hanovia medium-pressure mercury lamp for 72 h, while a slow stream of air was bubbled through the solution. The precipitate was collected by vacuum filtration, washed with  $\text{H}_2\text{O}$ , and then air dried to yield **4** as yellow powder; yield: 90%; mp > 300 °C.  $^1\text{H NMR}$  (DMSO- $d_6$ ):  $\delta$  = 7.75 (m, 4 H), 8.32 (d,  $J$  = 7.8 Hz, 2 H), 8.81 (s, 2 H), 8.97 (d,  $J$  = 7.5 Hz, 2 H), 12.3 (br s, 2 H NH).

Anal. Calcd for  $\text{C}_{24}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$ : C, 67.91; H 2.85; N, 6.60. Found: C, 67.30; H 2.59; N, 6.69.

#### 6,9-Dichlorobis[1]benzothieno[2,3-*c*;3',2'-*i*][1,10]phenanthroline (5)

A suspension of **4** (0.42 g, 1 mmol) in  $\text{POCl}_3$  (15 mL) was heated at reflux for 24 h. The reaction was allowed to cool to r.t. and then poured slowly into ice (200 mL). The resulting liquid slurry was then stirred for 0.5 h and allowed to stand overnight. Vacuum filtration yielded a greenish-yellow solid, which crystallized from DMF to give yellow crystals; yield: 85%; mp > 300 °C.

$^1\text{H NMR}$  (DMSO- $d_6$ ):  $\delta$  = 7.85 (m, 4 H), 8.40 (d,  $J$  = 7.5 Hz, 2 H), 9.16 (d,  $J$  = 7.5 Hz, 2 H), 9.42 (s, 2 H).

Anal. Calcd for  $\text{C}_{24}\text{H}_{14}\text{Cl}_2\text{N}_2\text{S}_2$ : C, 61.94; H 3.03; N, 6.02. Found: C, 61.90; H 2.81; N, 6.23.

#### Bis[1]benzothieno[2,3-*c*;3',2'-*i*][1,10]phenanthroline (6)

A mixture of **5** (0.23 g, 0.05 mmol), KOH (0.1 g), MeOH (20 mL), DMF (300 mL), and 10% Pd/C (0.1 g) was hydrogenated at atmospheric pressure at r.t. for 24 h. The catalyst was removed by filtration and the filtrate was evaporated to dryness in vacuo. The residual solid was washed with  $\text{H}_2\text{O}$  then filtered. The resulting solid was crystallized (EtOH–DMSO) to give compound **6** as yellow crystals; yield: 50%; mp > 300 °C.

$^1\text{H NMR}$  (DMSO- $d_6$ ):  $\delta$  = 7.80 (m, 4 H), 8.38 (d,  $J$  = 7.2 Hz, 2 H), 9.13 (d,  $J$  = 7.2 Hz, 2 H), 9.37 (s, 2 H), 9.83 (s, 2 H).

$^{13}\text{C NMR}$  (DMSO- $d_6$ ):  $\delta$  = 141.89, 128.91, 126.87, 126.62, 124.94, 124.02 (6 CH).

HRMS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{13}\text{N}_2\text{S}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 393.0515; found: 393.0516.

Anal. Calcd for  $\text{C}_{24}\text{H}_{12}\text{N}_2\text{S}_2$ : C, 73.44; H 3.08; N, 7.14. Found: C, 73.39; H 2.87; N, 7.23.

#### Acknowledgment

The authors thank the NSF for the purchase of the NMR instrument (grant no. 9980793) and Idaho State University and Fulbright Commission of Egypt for providing expenses for T.A.E.

## References

- (1) (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) Crutchley, R.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276. (c) Crutchley, R.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129. (d) Balazani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: England, **1991**, 161–190. (e) Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1434.
- (2) (a) Halverson, A. P.; Castle, L. W.; Castle, R. N. *J. Heterocycl. Chem.* **1996**, *33*, 179. (b) Halverson, A. P.; Castle, L. W. *J. Heterocycl. Chem.* **1996**, *33*, 727. (c) Halverson, A. P.; Castle, L. W. *J. Heterocycl. Chem.* **1996**, *33*, 119.
- (3) Gulevskaya, A. V.; Serduke, O. V.; Pozharskii, A. F.; Besedin, D. V. *Tetrahedron Lett.* **2003**, *39*, 7669.