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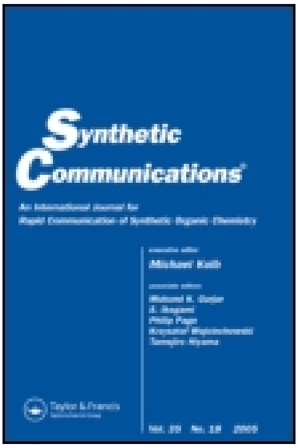

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis and Structure of a Novel Alkynyl-Containing Disulfide Compound as Cathode Materials for Secondary Lithium Batteries

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Accepted author version posted online: 15 Aug 2013.Published online: 11 Oct 2013.

To cite this article: Zuxi Jin , Yunguo Lu , Shixi Li & Zaoying Li (2014) Synthesis and Structure of a Novel Alkynyl-Containing Disulfide Compound as Cathode Materials for Secondary Lithium Batteries, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 44:1, 82-88, DOI: 10.1080/00397911.2013.789526

To link to this article: http://dx.doi.org/10.1080/00397911.2013.789526

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Synthetic Communications®, 44: 82–88, 2014

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2013.789526

SYNTHESIS AND STRUCTURE OF A NOVEL ALKYNYL-CONTAINING DISULFIDE COMPOUND AS CATHODE MATERIALS FOR SECONDARY LITHIUM BATTERIES

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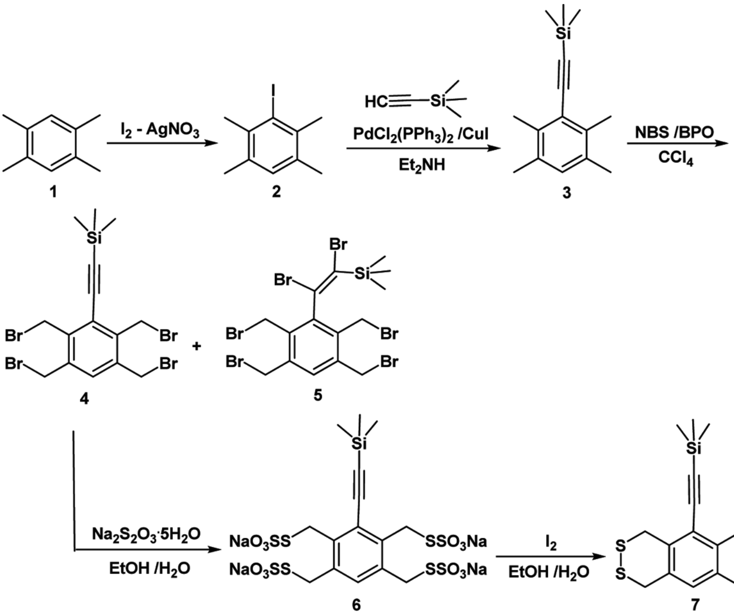
GRAPHICAL ABSTRACT



Abstract *A novel alkynyl-containing disulfide compound, 5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracen (TMSEDTTA), was synthesized. The structures of the target compound and the intermediates have been identified by* ^1H *NMR,* ^{13}C *NMR, mass spectrometry, Fourier-transform infrared, Raman spectra, x-ray photoelectron spectroscopy, and elemental analysis. In addition, the structure of (Z)-(1,2-dibromo-2-(2,3,5,6-tetrakis(bromomethyl)phenyl)vinyl)trimethylsilane* ***(5)*** *was determined by single x-ray analysis.*

Received January 28, 2013.

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Keywords Alkylbromination; disulfide; synthesis; thioesterification

INTRODUCTION

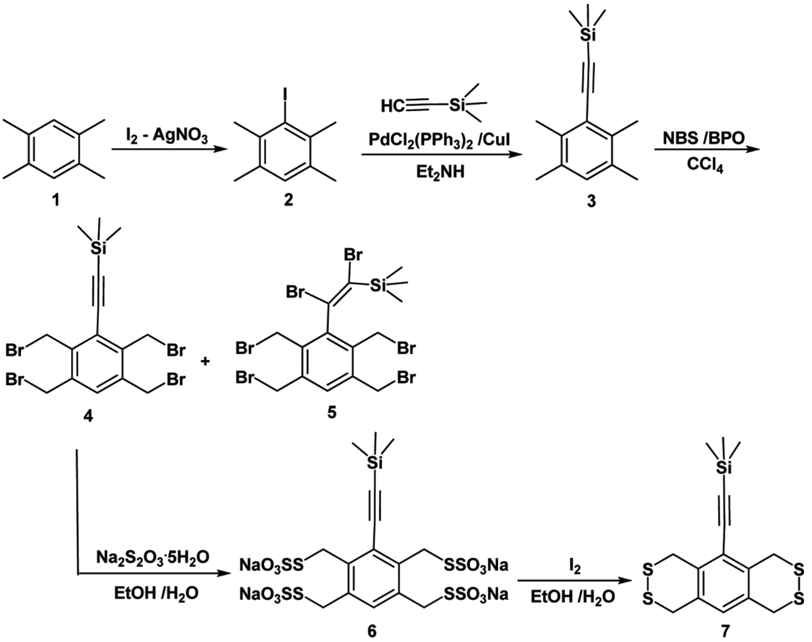
Since the 1980s, organodisulfide compounds have attracted research interest as positive active materials that have large energy density and are lightweight, low cost, and environmentally benign for high-power and lightweight lithium secondary batteries.[1] The disulfide bond (S-S), providing a reversible two-electron reaction during oxidation and reduction ($RS\text{-}SR + 2e^- = 2RS^-$), is the key moiety contributing high specific capacity to the organodisulfide compounds in the batteries.[2,3] At the same time polyphenylacetylene, one of the most promising intrinsically conducting polymers because of its straightforward polymerization, chemical and environmental stability, and relatively high conductivity, has been widely studied for applications in electronic and optical devices.[4,5] According to our previous studies and related reports,[6,7] the most effective approach for increasing practical specific capacity and cycling stability is to combine the S-S bond with the side chain of some kind of conducting polymer. The modification in the structure not only enables the catalysis of the backbone chain on the redox process of disulfides, it also brings about an effective inhibition of the loss of sulfur in the electrolyte during charging and discharging.[8] The depolymerized "monomer" after discharge was in fact a polymer and thus could provide an improved recombination efficiency of the S-S bond to enhance the cycling stability of this cathode material.

In this article, we designed, synthesized, and characterized a new phenylacetylene derivative, which has two condensed aliphatic rings containing two disulfur bonds. Its high disulfide density and intramolecular S-S bonds can lead to the promise of high effectivity as a potential battery material.

DISCUSSION

The total synthesis for the target compound 9-trimethyl silane ethynyl-5, 8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracene **(7)** were achieved in four steps starting from 1,2,4,5-tetramethyl-benzene **(1)** as outlined in Scheme 1. First, the starting material **1** was converted to 3-iodo-1,2,4,5-tetramethylbenzene **(2)** in 90% yield, which was modified from the general method of iodination of aromatic substrates under solvent-free conditions using the $I_2/AgNO_3$ combination in a solid state.[9] Thus we avoided the difficulty of eliminating the disubstituted by-product and obtained the highly pure monoiodination **2**.

Next, a direct Sonogashira cross-coupling reaction of iodo-durene with terminal acetylenes has been achieved under the optimized conditions.[10] This transformation was performed in diethylamine solvent at 60 °C, affording good isolated yield (95%), but yield was only moderate in the case when triethylamine was used as solvent, despite the prolonged reaction time.



Scheme 1. Synthesis of compound **7**.

Silylated alkyne **3** was brominated to **4** by *N*-bromosuccinimide (NBS) in the presence of benzoyl peroxide (BPO) in 30% yield. Not only tetrabromination compound **4** but also the addition product **5** were synthesized in one pot, which has not been reported in the literature under similar reaction circumstances. We successfully grew a single crystal of **5** from $CHCl_3$/petroleum ether (PE) and submitted it to x-ray crystallography. The ORTEP drawing of compound **5** is shown in Fig. 1, and it can be seen that the molecule has a Z-olefin structure, which provides a possible synthetic method from alkynyl to bromination addition olefin. The relative crystal data are presented in the Supporting Material. To suppress the generation of compound **5**, we diluted the concentration of reaction mixtures by increasing the amount of solvent; meanwhile N-bromosuccinimide (NBS) was added in small portion at mild reflux.

Finally, the benzylic bromide **4** was then converted to sodium alkylthiosulfate **6** ($Na_2S_2O_3$, EtOH/H_2O, 80 °C) as an intermediate, which, without purification, was directly used to generate tricyclic structure **7** by the oxidation of I_2. This process can be more efficiently carried out in one pot without the necessity of isolating the thioesterification product. Sodium alkylthiosulfate (Bunte salts) has been reported as a generally used regent to form disulfide compound by reaction with I_2[11] or hydrogen peroxide.[12] In this case, we completed the reaction with iodine but failed with hydrogen peroxide. Furthermore, to prove the existence of compound **6**, this reaction was interrupted before the addition of iodine. After evaporating solvents, the residue was recrystallized with EtOH/H_2O to afford the analytically pure product, which subsequently has been characterized by Fourier transform (FT)–Raman, NMR, and mass spectrometry (MS). Based on its water solubility and

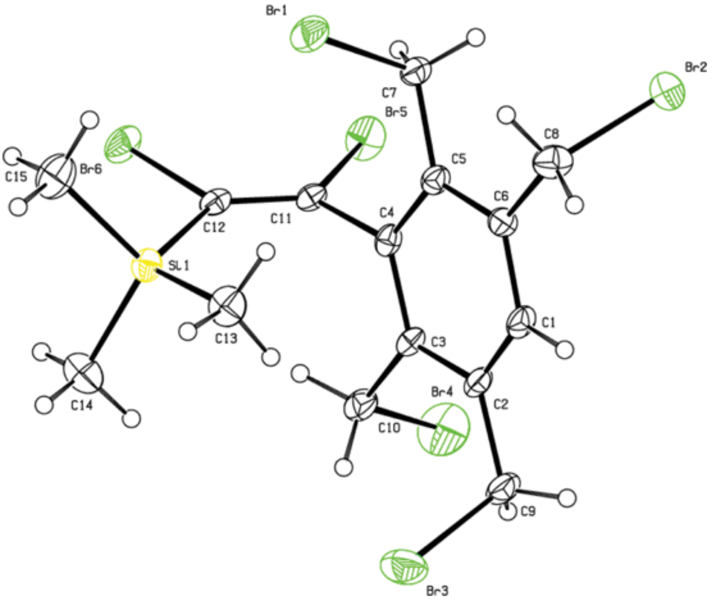


Figure 1. ORTEP drawing of the molecular structure of **5**. CCDC reference number 920770. (Figure is provided in color online.)

characterization data, it is indeed confirmed that the Bunte salts was formed in the procedure of cyclization.

Sulfur-rich compounds give very intense Raman spectra because the valence electrons in S-S bonds are highly polarizable[13] Therefore, Raman spectroscopy has always been a powerful research tool to characterize these compounds. In this work, the S-S stretching vibrations of compound **7** in Raman spectra were observed at 521 cm^{-1}, which was similar to the character of other disulfide compounds.[14] To confirm that the disulfide groups were well protected from further oxidation to sulfoxide or sulfone, X-ray photoelectron spectroscopy (XPS) spectra have been carried out to prove the preservation of S-S bonds. The bonding energy of S_{2p} is located at 163.7 eV, indicating the existence of disulfide bonds in compound **7**. The S_{2p} spectra also shows that sulfur in the target compound has only one valence state, in agreement with its structure.[15] The charge–discharge tests on the $Li/LiClO_4/$ 5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracen (TMSEDTTA) battery showed that the initial discharge capacity reached 330 mAh g^{-1}, which should include both contributions of phenylethynyl and S-S bonds of TMSEDTTA. However, the specific capacity of TMSEDTTA decreased dramatically, due to a rapid escape of the monomer from the cathode during the charge–discharge process. Nevertheless, the greater capacity and better cycle stability could be enhanced when the phenylethynyl polymer of unit TMSEDTTA was used as the cathode material.

In conclusion, the four-step synthesis of a novel alkynyl-containing disulfide compound, TMSEDTTA, has been developed. During the synthesis of target compounds, we utilized the solid-phase reaction to obtain monoiodination **2** with satisfactory conversion yield. Furthermore, three new compounds, **4, 5,** and **7**, were first prepared, and the single-crystal x-ray analysis of **5** confirmed its structure. The designed molecular is a potential material when polymerized and used as the cathode material of the secondary lithium batteries. The corresponding research work on polymerization is under way.

EXPERIMENTAL

Trimethyl((2,3,5,6-tetrakis(bromomethyl)phenyl)ethynyl)silane (4) and (Z)-(1,2-Dibromo-2-(2,3,5,6-tetrakis(bromomethyl)phenyl)vinyl)-trimethylsilane (5)

N-Bromosuccinimide (15.7 g, 88.4 mmol) was alternately added in small portions under nitrogen protection to a round-bottom Schlenk flask containing **3** (2.8 g, 12.3 mmol) and the benzoyl peroxide (0.6 g, 2.5 mmol) in CCl_4 (90 mL). The mixture was stirred at mild reflux for 12 h. After filtration of succinimide and removal of the solvent, the residue was purified by column chromatography. The resulting solid ($R_f = 0.3$) was recrystallized from petroleum ether (PE) to give pure **4** as white solid (30%). Mp: 128–129 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 1H), 4.86 (s, 4H), 4.57 (s, 4H), 0.34 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) (139.4, 137.6, 132.8, 126.3, 108.3, 98.2, 28.9, 27.2, −0.38. GC-MS (EI, m/z): 546 (M^+, 100). FT-IR (KBr) 2161 ($\nu_{C\equiv C}$), 1250 ($\nu_{C\text{-}Si}$), 680 ($\nu_{C\text{-}Br}$) cm^{-1}. The resulting solid ($R_f = 0.5$) was recrystallized from PE to obtain **5** as white solid (20%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 1H), 4.62–4.73 (m, 8H), −0.01 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) (141.7, 138.9, 137.4, 135.1, 134.6, 125.4, 28.9, 25.4, −0.38. FT-IR (KBr) 1630 ($\nu_{C=C}$) cm^{-1}.

Characterization Data of Compound 6

Mp: >300 °C. ^1H NMR (D_2O, 300 MHz): δ/ppm 7.45 (s, 1H, ph-H), 4.55 (s, 4H, *o*-ph-CH_2), 4.38 (s, 4H, *m*-ph-CH_2), 0.20 [s, 9H, -$Si(CH_3)_3$]. ^{13}C NMR (D_2O, 75 MHz): 137.4, 135.6, 133.8, 125.5, 109.1, 100.6, 36.3, 34.9, −0.76. FT-Raman: 2147 ($\nu_{C\equiv C}$), 1301 ($\nu_{C\text{-}Si}$), 722, 679 ($\nu_{C\text{-}S}$), 415 ($\nu_{S\text{-}S}$) cm^{-1}. MS (ESI, m/z): 743 (M-Na, 100).

9-Trimethyl Silane Ethynyl-5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracene (TMSEDTTA, 7)

The compound **4** (1.67 g, 3.06 mmol) and sodium thiosulphate (3.34 g, 13.5 mmol) were dissolved in 30 mL of anhydrous EtOH/H_2O (1:1). The mixture was refluxed with stirring until the solution was homogeneous. Iodine (1.61 g, 6.34 mmol) was then added in small portions until the color remained. Next, a sodium bisulfite solution was added to remove the excess iodine. After filtration, the brown precipitation was washed with water, dried in vacuum at 60 °C, and then extracted by 100 mL of boiling $CHCl_3$. Evaporation of solvent left the crude product, which was purified using silica-gel chromatography (PE/chloroform 3:0.2) to give 0.20 g (total yield 20%) of **7** as a white solid. Mp: 175–176 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 6.80 (s, 1H), 4.16 (s, 4H), 3.99 (s, 4H), 0.28 (s, 9H). ^{13}C NMR

(75 MHz, $CDCl_3$) (133.8, 131.7, 131.1, 124.5, 108.7, 99.6, 34.9, 32.6, −0.04. FT-IR (KBr) 758, 678 ($\nu_{C\text{-}S}$) cm^{-1}. FT-Raman 521 ($\nu_{S\text{-}S}$) cm^{-1}. Elem. anal.: Calcd. for $C_{15}H_{18}S_4Si$ (%): C, 50.80; H, 5.12; S, 36.17; Found(%): C, 50.84; H, 5.06; S, 36.50. ESI HRMS for $C_{15}H_{18}S_4Si[M+H]^+$: Found 352.9989. Calcd. 352.9977.

SUPPORTING INFORMATION

Full experimental detail, characterization data of compound **2** and **3**, copies of NMR spectra, crystallographic structure parameters, x-ray crystallographic information files (CIF) for compound **5** (CCDC 920770), S_{2p} of XPS, and the cycling specific capacity of TMSEDTTA can be found via the Supplementary Content section of this article's Web page.

ACKNOWLEDGMENT

We gratefully acknowledge financial support by the National Natural Science Foundation of China (No. 20872114).

REFERENCES

1. (a) Visco, S. J.; Maile, C. C.; Dejonghe, L. C.; Armand, M. B. A novel class of organosulfur electrodes for energy storage. *J. Electrochem. Soc.* **1989**, *136*, 661–664; (b) Liu, M. L.; Visco, S. J.; Dejonghe, L. C. Electrode kinetics of organodisulfide cathodes for storage batteries. *J. Electrochem. Soc.* **1990**, *137*, 750–759.
2. Naoi, K.; Kawase, K.; Mori, M.; Komiyama, M. Electrochemistry of poly(2, 2′-dithiodianiline): A new class of high energy conducting polymer interconnected with S-S bonds. *J. Electrochem. Soc.* **1997**, *144*, L173–L175.
3. Li, J. X.; Zhan, H.; Zhou, L.; Deng, S. R.; Li, Z. Y.; Zhou, Y. H. Aniline-based polyorganodisulfide redox system of high energy for secondary lithium batteries. *Electrochem. Commun.* **2004**, *6*, 515–519.
4. Dhanalakshmi, K.; Sundararajan, G. Synthesis of conjugated polyphenylacetylenes with redox active ferrocenyl end-groups. *Polym. Bull.* **1999**, *42*, 683–688.
5. (a) García-Cañadas, J.; Lafuente, A.; Rodríguez, G.; Marcos, M. L.; Velasco, J. G. Mechanism of electropolymerization of phenylacetylene in propylene carbonate. *J. Electroanal. Chem.* **2004**, *565*, 57–64; (b) Wu, J.; Walker, V. E. J.; Boyd, R. J. A theoretical study of the structure and conductivity of polycytosineacetylene. *Chem. Phys. Lett.* **2011**, *506*, 243–247.
6. (a) Deng, S. R.; Kong, L. B.; Hu, G. Q.; Wu, T.; Li, D.; Zhou, Y. H.; Li, Z. Y. Benzene-based polyorganodisulfide cathode materials for secondary lithium batteries. *Electrochim. Acta* **2006**, *51*, 2589–2593; (b) Li, Y. J.; Zhan, H.; Kong, L. B.; Zhan, C. M.; Zhou, Y. H. Electrochemical properties of PABTH as cathode materials for rechargeable lithium battery. *Electrochem. Commun.* **2007**, *9*, 1217–1221.
7. (a) Cho, J. S.; Sato, S.; Takeoka, S.; Tsuchida, E. Synthesis of disulfide-containing aniline and copolymerization with aniline. *Macromolecules* **2001**, *34*, 2751–2756; (b) Amaike, M.; Iihama, T. Chemical polymerization of pyrrole with disulfide structure and the application to lithium secondary batteries. *Synth. Met.* **2006**, *156*, 239–243.
8. Kiya, Y.; Iwata, A.; Sarukawa, T.; Henderson, J. C.; Abruña, H. D. Poly[dithio-2,5-(1,3,4-thiodiazole)] (PDMcT)–poly(3,4-ethylenedioxythiophene) (PEDOT) composite cathode

for high-energy lithium/lithium-ion rechargeable batteries. *J. Power Sources* **2007**, *173*, 522–530.

9. Yusubov, M. S.; Tveryakova, E. N.; Krasnokutskaya, E. A.; Perederyna, I. A.; Zhdankin, V. V. Solvent-free iodination of arenes using iodine–silver nitrate combination. *Synth. Commun.* **2007**, *37*, 1259–1265.
10. Chinchilla, R.; Nájera, C. Recent advances in Sonogashira reactions. *Chem. Soc. Rev.* **2011**, *40*, 5084–5121.
11. Westlake, H. E.; Dougherty, G. The use of Bunte salts in synthesis, III: The preparation of aliphatic disulfides. *J. Am. Chem. Soc.* **1942**, *64*, 149–150.
12. Twiss, D. F. The action of hydrogen peroxide on the sodium alkyl thiosulphates. *J. Chem. Soc.* **1914**, *105*, 36–39.
13. Steudel, R. The chemistry of organic polysulfanes R-S_n-R ($n > 2$). *Chem. Rev.* **2002**, *102*, 3905–3945.
14. Deng, S. R.; Wu, L.; Wang, H.; Zhou, B.; Li, Z. Y.; Zhou, Y. H.; Wong, W. K.; Guo, J. P. Synthesis and structure of a novel disulfide-containing aniline. *Synth. Commun.* **2005**, *35*, 129–135.
15. Xue, L. J.; Li, J. X.; Hu, S. Q.; Zhang, M. X.; Zhou, Y. H.; Zhan, C. M. Anthracene-based organodisulfide positive active materials for lithium secondary battery. *Electrochem. Commun.* **2003**, *5*, 903–906.