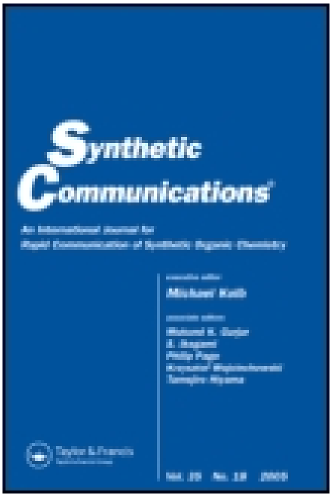

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# Synthesis and Structure of a Novel Disulfide-Containing Aniline

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# Synthesis and Structure of a Novel Disulfide-Containing Aniline

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**Abstract:** A novel disulfide-containing aniline, 5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracen-9-ylamine (**6**) was synthesized. The structures of the target compound and the intermediates have been identified by $^1$H NMR, MS, IR, Raman and elemental analysis. In addition, the structure of 9-Nitro-5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracene (**5**) was determined by single X-ray analysis.

**Keywords:** Alkylbromination, thioesterification, selective reduction, disulfide

A series of organodisulfide compounds[1,2] having two mercapto groups within the molecules are recently being considered as new energy storage materials in lithium batteries because of their high specific energy, whereby energy exchange occurs based on the reversible polymerization-depolymerization process ($2S^- \leftrightarrow S\text{-}S$). At the same time, polyaniline (PANI) as one of the most promising intrinsically conducting polymers due to its straightforward polymerization, chemical and environmental stability, and relatively high conductivity, has been widely studied for electronic and optical

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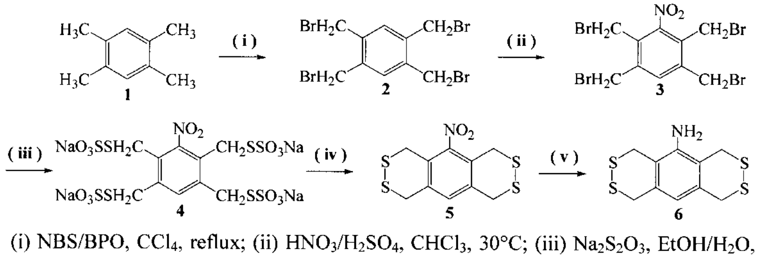
applications.[3] Since the 1990s, Naoi[4] found that the PANI could act as an effective electrocatalyst to speed up the redox of the disulfide, the researches on syntheses and properties of disulfide-containing aniline have been widely reported with relative satisfying results as a new kind of highly potential anode material.[5–7]

In this paper, we report the synthesis and structure of a new aniline derivative, which has two condensed aliphatic rings containing two disulfur bonds. Its high disulfide density and intramolecular S-S bonds can lead to a promising advantage of high effectivity as a potential battery material.[6]

The total synthetic steps for target compound 5,8-dihydro-1*H*,4*H*-2,3,6, 7-tetrathia- anthracen-9-ylamine (**6**) is achieved in four steps starting from 1,2,4,5-tetramethyl-benzene(**1**) as outlined in Scheme 1. Bromination of **1** (NBS, $CCl_4$, reflux) is followed by nitration of the bromide **2** ($HNO_3$, $CHCl_3$, 30°C) to afford the 1,2,4,5-tetrabromomethyl-3-nitrobenzene (**3**). In contrast, attempted nitration of **1** followed by bromination of the nitro compound failed to give the pure nitro compound **3**, a hardly isolated mixture of nitro benzylic bromide. It is noteworthy that during the course of nitration, the 3,6-dinitro-1,2,4,5-tetrabromomethyl-benzene was never obtained in this process. Either the mononitro compound results, or else unchanged starting material and oxidation product was generated, no matter how much the nitric acid was used.

The benzylic bromide **3** was then converted to a kind of sodium alkylthiosulfate (**4**) ($Na_2S_2O_3$, $H_2O$/EtOH, 80°C) as an intermediate which, without purification, was oxidized by $I_2$ in the same condition as above to form a tricyclic structure **5**. Sodium alkylthiosulfate (Bunte salts) has been reported as a generally used regent to form disulfide compound by reaction with iodine[8] and hydrogen peroxide.[9] In this case, we completed the reaction with iodine but failed with hydrogen peroxide. Furthermore, to prove the existence of the thioesterification product (**4**), the above reaction was interrupted before the addition of iodine, and the $^1H$ NMR($D_2O$) spectrum of the fine white solid mixture resulting from the evaporation of the above



(i) NBS/BPO, $CCl_4$, reflux; (ii) $HNO_3/H_2SO_4$, $CHCl_3$, 30°C; (iii) $Na_2S_2O_3$, EtOH/$H_2O$, reflux; (iv) $I_2$, EtOH/$H_2O$, reflux; (v) Fe, $NH_4Cl$, EtOH/$H_2O$, reflux.

*Scheme 1.*

solution was obtained. From its water solubility and the data[a] of its NMR spectrum, we can easily confirm the formation of this intermediate.

Finally, the nitro compound **5** was selectively reduced to amine **6** (Fe/ $NH_4Cl$, $H_2O$/EtOH, reflux), preventing the ring opening at the S-S bond. Fe/$NH_4Cl$ have been reported as a kind of specific reductant in neutral medium for the nitro group, along with other reducible group such as the nitrile and keto unaffected.[10] In this case, we successfully reduced the nitro group to the amino group with Fe/$NH_4Cl$ in a EtOH/$H_2O$ (1 : 1) mixed solution, without any change to disulfide bond. It is mentionable that if the medium of reduction changed to acid condition, the disulfide bond will be reduced to mercapto group.

Sulfur-rich compounds give very intense Raman spectra since the valence electrons in S-S bonds are highly polarizable.[11] Therefore, Raman spectroscopy has always been a powerful research tool in this area. In this work, the Raman spectra of compound **5** and **6**, both containing S-S bonds, were recorded. Their S-S stretching vibrations are observed at 522 and 525 $cm^{-1}$ respectively, which was similar to the character of other disulfide compounds.[12,13]

Our attempt of getting the single crystal of **6** failed, but we successfully grew a single crystal of **5** from $CHCl_3$ and submitted it to X-ray crystallography. The ORTEP drawing of the compound **5** is shown in Fig. 1, from which we can see clearly that the molecule has a nonplanar structure. The relative crystal data are presented in the Experimental section.

In conclusion, a four-step synthesis of a novel disulfide-containing aniline, 5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracen-9-ylamine(**6**) has been developed. During the synthesis of **6**, three new compounds, **3**, **5**, **6** were first prepared, and the single-crystal X-ray analysis of **5** confirmed its structure. The designed molecular is a kind of potential material when it is to be polymerized and used as the cathode material of the secondary lithium batteries. The corresponding research work on polymerization is under way.

## EXPERIMENTAL

1,2,4,5-Tetramethyl-benzene (**1**) and N-bromosuccinimide (NBS) were recrystallized from MeOH and $H_2O$, respectively. Other commercially available reagents were used without further purification, unless otherwise noted. All solvents used for extractions or reactions were dried according to standard procedures and kept over molecular sieves. 1,2,4,5-Tetrabromomethyl- benzene (**2**) was prepared according to literature[14] procedure. Melting-points were taken on a micro-melting apparatus and uncorrected.

[a] $^1H$ NMR($D_2O$) $\delta$ 7.63(s, 1H, ph-H), 4.37(s, 4H, *o*-ph-$CH_2$), 4.24(s, 4H, *m*-ph-$CH_2$).

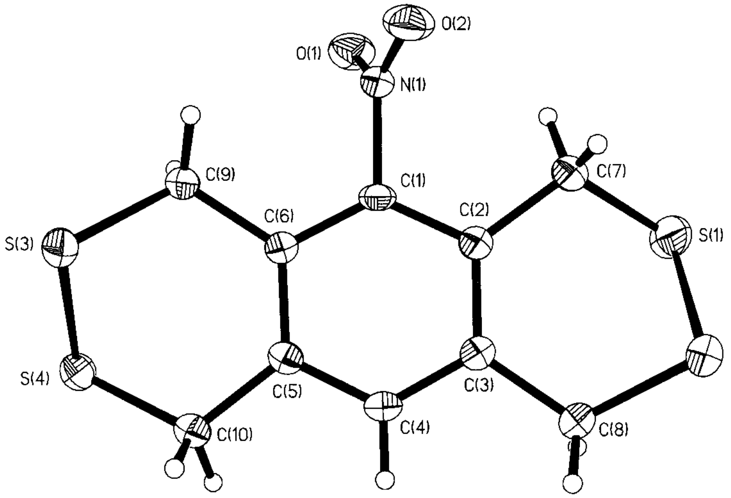


*Figure 1.* ORTEP Drawing of the molecular structure of **5**. CCDC reference number 235626.

NMR spectra were obtained on Varian Mercury-VX 300 spectrometers. Spectra were recorded in $CDCl_3$, using TMS as internal standard at 300 MHz for $^1H$ and 125 Hz for $^{13}C$ at 298 K if not stated otherwise; $\delta$ values are given in ppm and coupling constants are reported in Hz. FT-IR spectra were recorded on a Shimadzu Infred spectrophotometer (as KBr disc, values in $cm^{-1}$). Raman spectra were recorded on a NEXUS670 spectrophotometer. Mass spectra were obtained on a Thermo Finnigan TRACE MS PLUS (EI) and Finnigan LCQ advantage (electrospray). The element analyses were measured with a Finnigan FLASH 1112 SERIES EA. The crystal data were collected with a Bruker AXS SMART 1000 CCD. Chromatographic separations were performed using silica gel G (200–300 mesh, Qingdao, China).

### 1,2,4,5-Tetrabromomethyl-3-nitrobenzene (3)

12.6 g (196 mmol) of fuming nitric acid was added over 10 min into a magnetically stirred mixture of 9.0 g (20 mmol) **2** in 120 mL of $CHCl_3$ and 90 mL of 98% $H_2SO_4$ at 0°C. After heating at 30°C for 4 h, the reaction mixture was cooled to room temperature and poured into a separatory funnel to remove the mixed acid layer, and the upper organic layer was immediately washed with 10% NaOH and $H_2O$ and dried over $MgSO_4$. Removal of the solvent gave a white solid residue, which was recrystallized from $CHCl_3$/EtOH to afford 4.5 g (46%) of **2**, mp 187–188°C, $^1H$ NMR ($CDCl_3$) $\delta$ 7.55(s, 1H, ph-H), 4.62(s, 4H, *o*-ph-CH$_2$), 4.47(s, 4H, *m*-ph-CH$_2$), FT-IR(KBr) 3038, 2921($\nu_{\text{C-H}}$), 1525, 1327($\nu_{\text{N=O}}$), 601($\nu_{\text{C-Br}}$) cm$^{-1}$, Anal. for $C_{10}H_9Br_4NO_2$ Calcd: C, 24.27; H, 1.83; N, 2.83, Found: C, 24.22; H, 1.83; N, 2.80.

### 9-Nitro-5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracene (5)

The compound **3** (2.0 g 4.0 mmol) and sodium thiosulphate (4.0 g 16.1 mmol) were dissolved in 80 mL of EtOH/H$_2$O (1 : 1). The mixture was refluxed with stirring until the solution was homogeneous. The iodine was then added in small portions until the color remained. Then a sodium bisulfite solution was added to remove the excess iodine. After filtration, the yellow precipitation was washed with water and then dried in vacuum at 80°C and then extracted by 100 mL of boiling CHCl$_3$. Evaporation of solvent left a yellow solid, which was purified using silica gel chromatography (chloroform/petroleum ether 10 : 3) to give 0.64 g (53%) of **5** as a yellow solid: mp 136–137°C; $^1$H NMR (CDCl$_3$) $\delta$ 6.99(s, 1H, ph-H), 4.05(s, 4H, *o*-ph-CH$_2$), 3.85(s, 4H, *m*-ph-CH$_2$); FT-IR (KBr) 2960, 2914($\nu_{\text{C-H}}$), 1532, 1363($\nu_{\text{N=O}}$) cm$^{-1}$; Raman 525($\nu_{\text{S-S}}$) cm$^{-1}$; ESMS *m*/*z* 301.6[M-H]$^+$; Anal. for $C_{10}H_9NO_2S_4$ Calcd: C, 39.58; H, 2.99; N, 4.62, Found: C, 39.64; H, 3.02; N, 4.58.

### 9-Amino-5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracene (6)

A hot solution of 0.2 g (0.66 mmol) of **5** in 80 mL of EtOH was added to a refluxing mixture of 7.0 g(125 mmol) of iron powder and 6.0 g (112 mmol) of NH$_4$Cl in 80 mL of H$_2$O under nitrogen atmosphere. After heating at reflux for 4 h, the reaction mixture was cooled and filtered and the filtrate was extracted with CHCl$_3$ (3 × 30 mL), the combined extracts were washed with H$_2$O (3 × 30 mL), dried over Na$_2$SO$_4$ and purified using silica gel chromatography (CHCl$_3$) to give 0.14 g (78%) of 6 as a light yellow solid: mp 126°C (dec); $^1$H NMR (CDCl$_3$) $\delta$ 6.36(s, 1H, ph-H), 4.01(s, 4H, *o*-ph-CH$_2$), 3.72(s, 4H, *m*-ph-CH$_2$), 3.61(s, 2H, broad, NH$_2$); $^{13}$C NMR (CDCl$_3$) $\delta$ 142.8, 131.4, 122.0, 116.4, 36.2, 28.4; FT-IR(KBr) 3463, 3386, 1625($\nu_{\text{N-H}}$) cm$^{-1}$; Raman 522($\nu_{\text{S-S}}$) cm$^{-1}$; MS (EI) 273[M]$^+$; Anal. for $C_{10}H_{11}NS_4$ Calcd: C, 43.92; H, 4.05; N, 5.12, Found: C, 44.05; H, 4.07; N, 5.08.

### X-Ray Crystallographic

The crystal structures of compound **5** were determined using data collected at 293 K with Mo K$_\alpha$ radiation on a Bruker AXS CCD diffractometer. The structure was solved by direct methods (SHELXS-97) and refined using full-matrix least-squares on $F^2$.

Slight yellow crystal of **5** was obtained by slow crystallization ($CHCl_3$) at 0–4°C over 1 week. A crystal of dimensions $0.20 \times 0.20 \times 0.10\,mm^3$ was selected and found to crystallize in the orthorhombic space group *Pbca,* $a = 14.9439(10)\,Å$, $b = 8.1770(6)\,Å$, $c = 19.8869(13)\,Å$, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 2430.1(3)\,Å^3$, $Z = 8$, $d_{calc} = 1.659\,Kg\,m^{-3}$,$T = 293\,K$. 13674 reflections were measured, 2911 unique ($R_{int} = 0.0501$). The final $wR(F^2)$ was 0.0898 for all data, $R_1(F)$ was 0.0373 where $I > 2\sigma(I)$. Goodness of fit on $F^2$ is 1.016.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the reference number CCDC 235626. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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