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A Highly Electron-Deficient Analogue of Aniline, Soluble Oligomers, and Their Redox Properties

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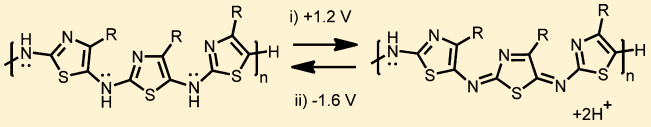
Supporting Information

ABSTRACT: The synthesis and electrochemical oxidative coupling of a highly electron-deficient analogue of aniline results in the formation of soluble electron-deficient oligomers. Oligomers undergo related oxidation and reduction processes that are separated by a wide potential range. The mechanism behind this behavior is examined by cyclic voltammetry, optical absorption spectroscopy, ^{1}H NMR spectroscopy, and density functional theory calculations. Mesomeric isomerization of the oxidized oligomers leads to a very stable oxidized state that requires a large (2.8 V) overpotential to return to the neutral form.



INTRODUCTION

The availability of new conjugated polymers has continually grown since the discovery of conducting polyacetylene, but most examples still contain very similar building blocks.[1] Efforts focus on developing electron-rich conjugated polymers because of their ease of synthesis and more robust electrical and electrochemical properties. There are comparatively few examples of electron-deficient materials described in the literature, most of which are difficult to prepare or have other significant drawbacks including poor solubility.[2] There is however a need to synthesize and study new electron-deficient materials since they may have advantageous properties. These materials may be useful for new n-type materials/devices, materials that require stability toward photooxidation, or have fundamentally intriguing properties.[3]

Poly- and oligoanilines are among the most intensively studied conjugated materials due to their highly conductive salt form and electrochemical properties.[4] The electrochemical activity of polyaniline exhibits two distinct and fully reversible redox peaks in a standard electrochemical experiment (cyclic voltammetry). These peaks correspond to the transformation from the leucoemeraldine base to the emeraldine salt, and the transformation from the emeraldine salt to the pernigraniline base, respectively. Considering the ample recent literature focused on the electronic properties and device performance of oligo/polyaniline,[5] examining electron-deficient analogues of aniline is an important step in developing new materials and to gain insight into their electronic properties.

Herein, we describe the design, synthesis, and electrochemical characterization of a novel, soluble, and highly electron-deficient analogue of aniline: 2-amino-4-caproylthiazole, which undergoes oxidative coupling to form conjugated oligomers. The electron-withdrawing groups include the nitrogen within the thiazole ring and the carbonyl directly bonded to the conjugated backbone, which both add to the electron deficiency of the oligomer. An alkyl chain was also incorporated into 2-amino-4-caproylthiazole to prepare materials that remain soluble, allowing us to study the redox properties of the oligomers by a variety of techniques, while ruling out intermolecular interactions as well as the influence of morphology, which is not possible in the solid state. This technique has not been used prior to this study for other aminothiazole derivatives and leads to findings unreported for other poly-2-aminothiazoles. Oligomers of 2-amino-4-caproylthiazole have electrochemical properties notably different from those of polyaniline[3] or other thiazole-based copolymers.[6] Specifically, while 2-aminothiazole undergoes irreversable oxidative coupling[7] and poly-2-aminobenzothiazole[8] is irreversible reduced, we discover that oligomers of 2-amino-4-caproylthiazole possess a stable oxidatized state that persists over a wide potential range.

RESULTS AND DISCUSSION

The monomer chosen for this study is 2-amino-4-caproylthiazole (**3**) which is an alkylated 2-aminothiazole with an electron-withdrawing ketone functionality. The synthesis begins with 2-pentyl-1,3-dithiane (Scheme 1), a propanedithiol protected form of hexanal.[9] The choice of protecting group is noteworthy because the protecting group must be stable toward lithiation in contrast to other similar protecting groups.[10] In the first step, 2-pentyl-1,3-dithiane is treated with *n*-hexyllithium (in dry THF) at room temperature, the reaction mixture is cooled to −78 °C, and methyl chloroacetate is slowly added. The temperature is maintained at −78 °C during methyl chloroacetate addition, to increase reaction selectivity between the organolithium reactant and the methyl chloroacetate ester, and then the mixture is gradually warmed to room temperature with stirring. After isolation and work up, this procedure affords intermediate 2-chloro-1-(2-pentyl-1,3-dithian-2-yl)ethanone

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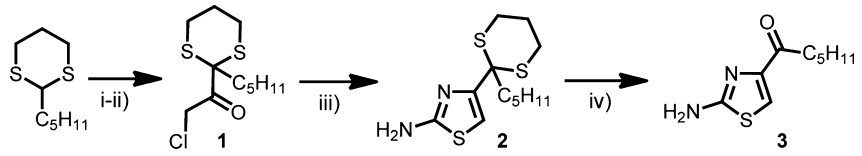
Scheme 1. Synthesis of 2-Aminothiazole Derivative 3[a]



[a]Reagents and conditions: (i) 2.3 M hexyllithium, anhydrous THF/hexanes, argon, 25 °C, 0.5 h); (ii) methyl chloroacetate, −78 °C (52%); (iii) thiourea, *n*-PrOH, 55 °C, 1 h, 25 °C, 12 h (53%). (iv) 9.71 M $H_2O_{2(aq)}$, I_2, MeOH, 6 h (28%).

(**1**). In the next step, 4-(2-pentyl-1,3-dithian-2-yl)thiazol-2-amine (**2**) is prepared by treating **1** with thiourea in a manner that is analogous to the Hantzsch synthesis procedure.[11] Finally, **3** is prepared by treatment with hydrogen peroxide and iodine to remove the propanedithiol protecting group.[12]

Compounds **2** and **3** are isolated as highly soluble crystalline solids. Crystals suitable for X-ray analysis are obtained by slow evaporation from *n*-butanol or ethyl acetate/hexanes (50/50; v/v), for **2** and **3**, respectively, and their molecular structures are confirmed (Figure 1 and Supporting Information).

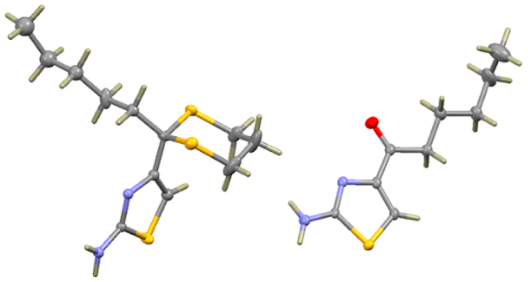


Figure 1. The crystal structure of **2** (left) and **3** (right). Ellipsoids are drawn at the 50% probability level.

The electrochemical oxidative coupling of **3** is carried out in an acetonitrile solution containing 0.5 M tetrabutylammonium hexafluorophosphate using a platinum gauze working and a platinum wire counter electrode. A silver wire is used as a pseudoreference electrode, and all potentials are reported vs ferrocene/ferrocenium. Oxidative scanning between −0.5 V and +1.8 V reveals a broad oxidation, and repeated scanning within this potential range results in a decrease in current (Figure 2a). This prompted us to widen the potential window, to further examine the oxidation and reduction behavior of **3**. In a second experiment, oxidative scanning between −0.5 V and +1.8 V is followed by a reductive sweep to −1.9 V and then back to −0.5 V (Figure 2). During this experiment, we observe the oxidation peak shift to lower potential. An intriguing reductive peak is also observed at very negative potentials (−1.6 V). Repeated scanning caused both of these peaks to increase and the electrochemical solution to change from colorless to orange. Spectroelectrochemical (SEC) measurements (Figure 3) reveal that the absorption peak red-shifts into the visible region of the spectrum. Note that reactions in the SEC cell proceed faster because of the smaller volume. All of these observations are consistent with the oxidative coupling of heterocycles (Scheme 2).[13] After 60 cycles (between +1.8 V and −1.9 V), repeated scanning does not produce significant changes in the voltammograms, indicating that the oxidative coupling reaction to produce **4** is complete. Oligomers of **4** contain approximately seven repeat units, as determined by ^{1}H NMR end-group analysis (NMR characterization is described

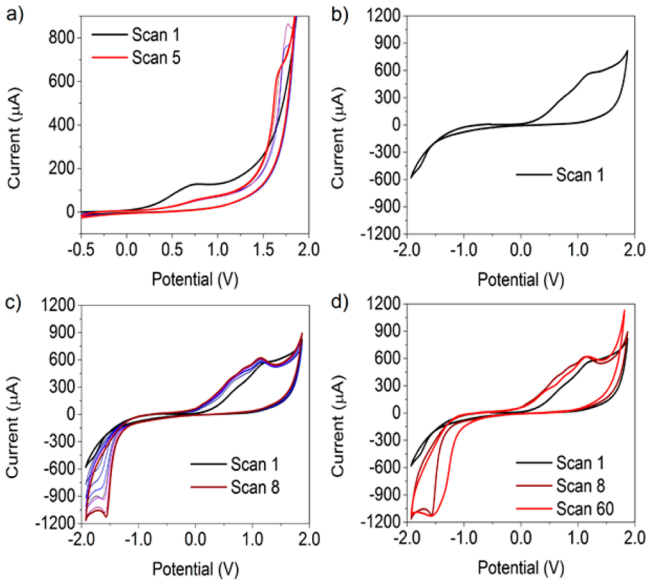


Figure 2. Electrochemical coupling of **3**. Cyclic voltammograms for (a) oxidation only. (b−d) Oxidation and reduction.

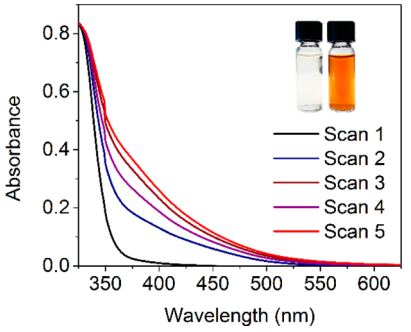
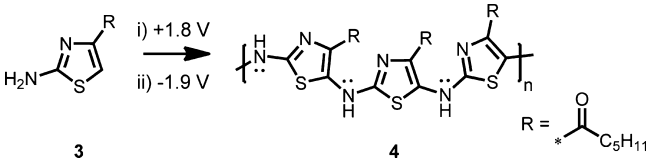


Figure 3. Spectroelectrochemistry of **3** and **4** at −0.5 V (vs fc) after reduction with the electrochemical solution of **3** (colorless) and **4** (orange).

Scheme 2. Electrochemical Synthesis of Oligomer 4 (potentials vs fc/fc$^+$)



below). These oligomers remain soluble and do not adhere to the surface of the working electrode as typically observed for insoluble polymers.

The large difference in potential for these processes at +1.2 V and −1.6 V is a noteworthy property that has not previously

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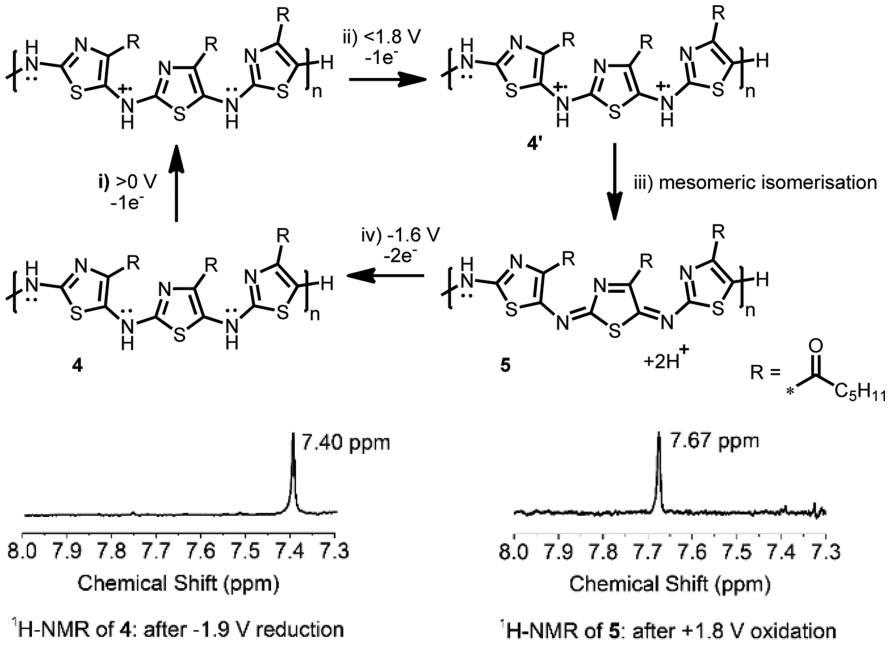

^{1}H-NMR of **4**: after -1.9 V reduction

^{1}H-NMR of **5**: after +1.8 V oxidation

Figure 4. Proposed mechanism for the oxidation, mesomeric isomerization, and reduction of **4** with the corresponding chemical shifts observed in the ^{1}H NMR.

been examined in solution; thus, we examined the mechnism behind this process. The voltammogram of **4** contains one broad oxidation peak with several shoulders, indicating a multistep oxidation between 0 and +1.8 V. In contrast, the reduction at −1.6 V is more concerted, occurring over a much narrower potential window and with only one clearly defined peak. This redox activity is unlike the reversible multistep oxidations of the more electron-rich analogue, polyaniline.[4] Furthermore, oxidized forms of polyaniline have a broad optical absorption that stretches into the near-infrared (NIR) spectrum, which is the result of their partially open-shell electronic structure.[14] A similar NIR absorbance is not observed during the spectroelectrochemical analysis of **4** (Figure 3). These differences between **4** and polyaniline are consistent with electron-withdrawing inductive effects that can destabilize an open-shell upon oxidation.[15] Thus, we propose that oxidized **4** rapidly isomerizes to a closed-shell diimine structure (**5**) that is energetically more favorable than open-shell structures such as **4′** (Figure 4). This rapid isomerization gives rise to an oxidation process that is not reversible within narrow scan windows. Unrestricted density functional theory calculations [B3LYP 6-31(d); singlet multiplicity] predict that the closed-shell electronic structure **5** is most favorable and higher spin states are less favorable (see Supporting Information).[16] These calculations support that **5** is the minimum energy electronic configuration upon oxidation. It is only when scanned to excessively negative potentials that oxidized isomer **5** can be converted back to neutral **4**.

To investigate this mechanism, the contents of the electrochemical cell obtained from the oxidation−reduction cycles were analyzed by ^{1}H NMR (Figure 4 and see Supporting Information). After reduction to −1.9 V, there is a single peak in the aromatic region at 7.40 ppm that is assigned as the end group of **4**. The absence of other end group peaks indicates a clean reductive process through electrochemical synthesis. A broad peak at 5.82 ppm is assigned to the amino groups in the reduced form. Comparative integration between this peak and the end group peak reveals that approximately seven monomer units have been coupled together during the synthesis. Oxidation to +1.8 V results in a single peak in the aromatic region; however, this peak occurs at 7.67 ppm and is distinct from that of **4**. We assign this peak to oxidized isomer **5**. The observation of an aromatic peak indicates that **5** is diamagnetic, verifying the closed-shell electronic structure. The downfield shift of this peak is consistent with the electron-deficient diimine form proposed for **5**. These findings support that two distinct, stable electronic isomers can be obtained from either oxidation to +1.8 V or reduction to −1.9 V.

We also examined the products from the chemical oxidation[8] of **3** in acetonitrile by ^{1}H NMR and found that chemical synthesis produces a mixture of **4** and **5** as indicated by the two distinct peak reagions observed in the aromatic region of the spectrum (see Supporting Information). One occurs between 7.87 and 7.72 ppm and is attributed to oxidized forms of the oligomer **5**. The second peak appears at 7.37 ppm and is attributed to isomer to **4**. This peak is in a location similar to that of the monomer **3** but has now become broader. Further analysis of the end groups indicates that 40% of the oligomers are in the reduced state and 60% are oxidized. These findings are consistent with the mixed oxidation states found in related polymers prepared by chemical synthesis.[14] The chemically prepared oligomer is also characterized by gel permeation chromatography (GPC) and supports that, on average, four thiazole units are linked together in reference to a polystyrene standard (M_n: 522 g/mol, M_w 710 g/mol, PDI: 1.36).

We examined the stability of the redox processes of **4** and **5** through repeated CV scanning between +1.8 V and −1.9 V at 100 mV/s to further support our proposed mechanism (Figure 5a). The oxidative scan consistently reaches 590 μA at the maximum peak potential (+1.2 V) for 10 cycles (Figure 5c). For each of these cycles, 3.0 μC is expended upon oxidative sweeping to convert **4** into **5** (Figure 5e). Furthermore, the charge that is associated with the oxidative and reductive peaks at +1.2 V and −1.6 V are very similar (3.0 μC and 3.4 μC,

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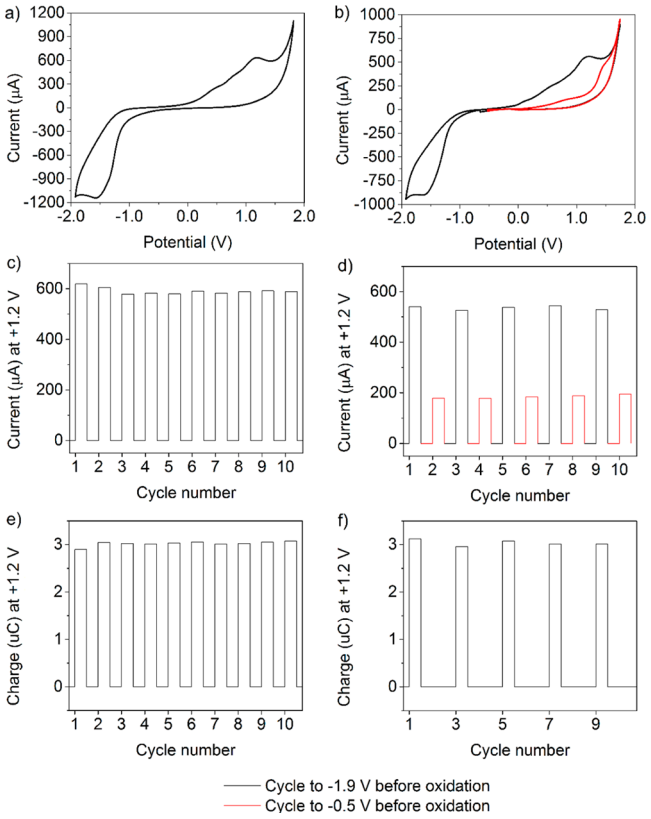

Figure 5. Cyclic voltammograms obtained from (a) cycling between −1.9 V and +1.8 V (CV-1) and (b) switching between −1.9 V and +1.8 V and −0.5 V to +1.8 V cycles (CV-2). Current measured at +1.2 V for repeated cycling of (c) CV-1 and (d) CV-2. Charge expended converting **4** to **5** for repeated cycling of (e) CV-1 and (f) CV-2.

respectively), confirming that a similar amount of material is oxidized and then reduced. In a second experiment, the first sweep, a reduction scan to −1.9 V, produces **4**. This is followed by oxidation to +1.8 V to produce **5**. This cycle is followed by a second reductive sweep to −0.5 V, which is not a low enough potential to reduce the oligomer to **4**. The oligomer remains in its oxidized form **5** and is subjected to another oxidative scan to 1.8 V, which results in a significantly lower current (Figure 5b). Cycling back to −1.9 V is then used to reset the process. For 10 of the scans described above, the current consistently switches between 540 and 180 μA at +1.2 V (Figure 5d). The electric charge expended upon oxidative sweeping to convert **4** back into **5** remains constant (3.0 μC) for each cycle (Figure 5f). In either experiment, no current is lost in either the oxidative or reductive peaks upon repeated scanning, demonstrating that the two redox states are robust and do not lead to decomposition/reaction in solution.

CONCLUSIONS

In conclusion, 2-amino-4-caproylthiazole **3** has been synthesized, characterized, and coupled by electrochemical oxidation, forming novel electron-deficient conjugated oligomers. The oligomers display unique electrochemical properties, specifically two coupled processes, one oxidation and one reduction to the neutral form, that persist over a wide potential range. We demonstrate the stability of these processes by repeated cycling and switching experiments. This redox activity is unlike the reversible multistep oxidations of the more electron-rich analogue, polyaniline, and is consistent with electron-withdrawing inductive effects that destabilize the oxidized open-shell structure. These soluble oligomers of 2-amino-4-caproylthiazole provide insight into the electronic structure of highly electron-deficient oligomers/polymers.

EXPERIMENTAL SECTION

General Considerations. All reagents were purchased from commercial sources and were used as received unless otherwise noted. 2-Pentyl-1,3-dithiane was synthesized from hexanal and 1,3-propanedithiol according to literature procedures.[9]

Instrumentation and Methods. NMR spectra were recorded on a spectrometer operating at 400 MHz and chemical shifts are reported in ppm at ambient temperature and referenced to the residual chloroform solvent peak at 7.26 ppm for ^{1}H NMR and 77.36 ppm for ^{13}C NMR. HRMS were recorded using a direct analysis in real time (DART) ion source with positive ion polarity and a time of flight (TOF) mass analyzer.

Electrochemistry. Electrochemistry was performed using a standard three-electrode cell with a Pt gauze working electrode, a silver wire pseudoreference electrode, and a Pt wire counter electrode. All potentials were referenced to an internal ferrocene standard (added and analyzed after the reported scan). The electrolyte was a 0.5 M solution of tetrabutylammonium hexfluorophosphate in acetonitrile. A 100 mV/s scan rate was used in all cyclic voltammetry. For spectroelectrochemical and ^{1}H NMR measurements, controlled potential electrolysis was used with a quartz cuvette, fitted with the same electrodes and electrolyte solution.

Density Functional Theory Calculations. Geometry optimizations were performed using the Gaussian 09 program, employing the Becke three-parameter hybrid functionals Lee−Yang−Parr (B3LYP) level of theory and the 6-31G(d) basis set.[16] The alkyl chains were replaced with methyl groups to reduce processing time.

Synthesis of 2-Chloro-1-(2-pentyl-1,3-dithian-2-yl)ethanone (1). 2-Pentyl-1,3-dithiane (12.4 g, 0.0650 mol) was added to a 500 mL three-neck round-bottom flask fitted with a low temperature thermometer, septum, and gas inlet. Dry THF (100 mL) was added to the flask, and the contents were placed under an argon atmosphere while stirring for 10 min. A 2.3 M solution of hexyllithium in hexanes was added (100 mL, 3.5 equiv) at room temperature, and the mixture was stirred for 30 min. The mixture was cooled to −78 °C, and methyl chloroacetate was added slowly while maintaining the −78 °C temperature. After methyl chloroacetate addition was complete, the reaction was allowed to warm to room temperature with constant stirring and then quenched with water (50 mL). The organic solvent was removed by rotary evaporation, and the contents of the flask were extracted into ethyl acetate, washed with water, dried with $MgSO_4$, and concentrated. The product was purified by column chromatography using 5% ethyl acetate in hexanes to yield 9.03 g (52%) of the title compound. Note: 4.40 g of unreacted 2-pentyl-1,3-dithiane was also recovered. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.51 (2H, s), 2.98 (2H, m), 2.63 (2H, m), 2.07 (1H, m), 1.95 (2H, m), 1.83 (1H, m), 1.27 (6H, m), 0.86 (t, 3H, J = 6 Hz) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 195.3, 60.7, 44.2, 38.3, 31.75, 27.8, 24.4, 24.0, 22.1, 13.8 ppm. DART-HRMS mass for $C_{11}H_{20}ClOS_2$ [M + H]: calculated 267.06441 Da, measured 267.06410 Da.

Synthesis of 4-(2-Pentyl-1,3-dithian-2-yl)thiazol-2-amine (2). Thiourea (2.58 g, 0.0339 mol) was dissolved in *n*-propyl alcohol (100 mL) and combined with compound **1** (9.03 g, 0.0338 mol). The mixture was stirred at 55 °C for 1 h and at room temperature for 12 h. This mixture was passed through a short basic alumina column using methanol as the eluent and concentrated to afford a white precipitate. The precipitate was collected by vacuum filtration and washed with hexanes (40 mL × 2) to give 5.18 g (53%) of the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.75 (1H, s), 4.92 (2H, s), 2.92 (2H, m), 2.74 (2H, m), 2.10 (4H, m), 1.35 (6H, m), 0.86 (3H, m) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 166.7, 153.2, 108.0, 55.2, 42.3, 31.7, 27.7, 25.4, 23.6, 22.4, 14.0 ppm. DART-HRMS mass for $C_{12}H_{21}N_2S_3$ [M + H]: calculated 289.08669 Da, measured 289.08674 Da.

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Synthesis of 2-Amino-4-caproylthiazole (3). Compound **2** (2.88 g, 0.0100 mol) was combined with a solution of peroxide (9.71 M, 4.12 mL) and I_2 (0.127 g, 0.496 mmol) in methanol (289 mL). The mixture was stirred for 6 h, concentrated to 40 mL by rotary evaporation, and filtered. The filtrate was combined with DCM (350 mL), washed with distilled water, dried with $MgSO_4$, and concentrated. Column chromatography, eluting first with 25% ethyl acetate in hexanes, followed by 50% ethyl acetate in hexanes, afforded 555 mg (28%) of a white crystalline solid, the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (1H, s), 5.49 (2H, s), 2.87 (2H, t, J = 6 Hz), 1.71 (2H, m), 1.35 (4H, m), 0.91 (3H, t, J = 8 Hz) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 194.6, 167.2, 151.2, 116.6, 39.5, 31.5, 23.9, 22.5, 13.9 ppm. DART-HRMS mass for $C_9H_{15}N_2OS$ [M + H]: calculated 199.09051 Da, measured 199.09022 Da.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds, crystallographic information, and density functional theory optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest

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