Synthesis of Bis[1,2]dithiolo[1,4]thiazines and a [1,2]Dithiolo[1,4]thiazine from Tertiary Diisopropylamines

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The reaction of *N*-(2-chloroethyl)diisopropylamine **1a** with S_2Cl_2 allows the selective one-pot preparation of the tricyclic 4-(2-chloroethyl) bisdithiolothiazines **2**−**4** or, by addition of phosphorus pentasulfide at a late stage in the reaction, of the dithiolothiazine **5**. The chloroethyl derivative **2** is also obtained from (2-diisopropylamino)ethanethiol **1b**, or its disulfide **1c**, with S_2Cl_2, in a rare conversion of a thiol or disulfide into the corresponding chloro compound. Compounds **2** and **5** are also obtained from *N*-(2-hydroxyethyl)diisopropylamine **1d**, though in much lower yields. The reaction of *N*-(2-phenylthioethyl) (**1e**) or *N*-(2-phthalimidoethyl)diisopropylamines **1f**,**g** affords bisdithiolothiazines **7**, **8**, **9**, and **11** and the dithiolopyrrole **10**. A coherent set of reaction pathways for the formation of these products is proposed. X-ray crystallography shows that the bisdithiolothiazine ring system of **2** is folded out of planarity about the thiazine N−S vector, with the *N*-chloroethyl group folded back over the thiazine ring with the chlorine atom lying above the thiazine sulfur atom; the dithiolothiazine ring system of **5** has the thiazine ring in a "sofa" conformation.

Introduction

The chemistry of various sulfur heterocycles such as thiophenes and 1,3-dithioles has been extensively studied since the discovery of their superconductivity[1] and optical and electronic switching properties.[2] Polysulfur−nitrogen heterocycles could be even better candidates for such behavior, if practical syntheses were available. We have studied the reactions of cyclic oximes with disulfur dichloride (sulfur monochloride), S_2Cl_2, in the presence of *N*-ethyldiisopropylamine (Hünig's base), to produce suitable materials for electronic or optical applications, and have discovered a simple route to some heterocyclic pseudoazulenes,[3] that constitute a new family of liquid crystalline materials,[4] and a one-pot synthesis of benzodithiazolones.[5] During this work we found that Hünig's base, a simple saturated tertiary amine, is converted in a one-pot reaction by S_2Cl_2 into the fully unsaturated tricyclic bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine ring system[6] or, at a higher temperature, into the bis[1,2]dithiolo-[4,3-*b*:3′,4′-*d*]pyrrole system[7] by selective sulfur extrusion from the thiazine. Only the isopropyl groups of Hünig's base reacted with S_2Cl_2, the ethyl group being unchanged.[8] This led us to consider the reactivity of functionalized ethyl groups, both to explore the scope of the reaction and possibly to intercept proposed intermediates on the long reaction pathway, by cyclizations involving the ethyl group substituents. In this way, we discovered that *N*-(2-chloroethyl)diisopropylamine may afford either 4-(2-chloroethyl)bisdithiolothiazines or, by addition of phosphorus pentasulfide at a late stage of the

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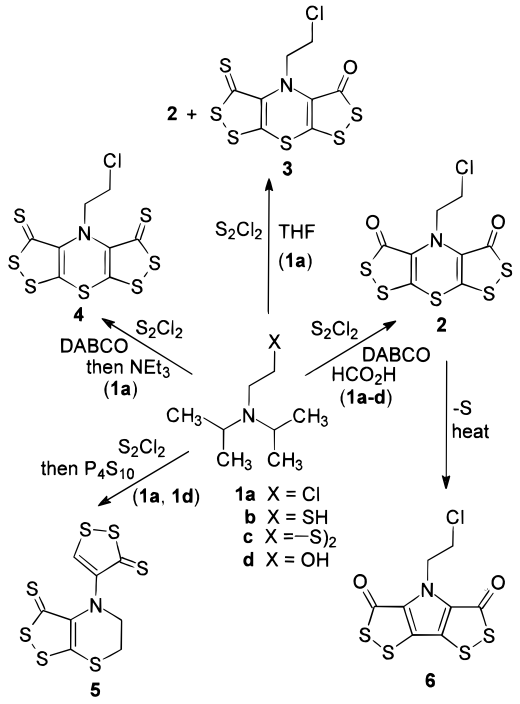
Scheme 1



reaction, a new dithiolothiazine derivative.[9] We have made a systematic study of these reactions to understand how the functionalization of the ethyl group in the starting material, and the reaction conditions, affect the nature of the final product. We now report precise conditions for the selective synthesis of each class of compounds, mechanistic proposals based on reaction pathways, and the structures and crystal packing obtained from X-ray diffraction analysis.

Results and Discussion

Preliminary experiments had shown that electron-withdrawing substituents in place of the ethyl group, as in *N*,*N*-diisopropylacetamide or *N*,*N*-diisopropylcyanamide, suppressed the reaction of the isopropyl groups with S_2Cl_2. We therefore selected the commercially available *N*-(2-chloroethyl)diisopropylamine **1a**, which is readily converted into the thiol **1b** and its disulfide **1c**,[10] and *N*-(2-hydroxyethyl)diisopropylamine **1d**. These compounds (1 equiv) were each treated with S_2Cl_2 (10 equiv) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (ca. 10 equiv) in 1,2-dichloroethane for 3 days at room temperature. Formic acid (20 equiv) was then added and the mixture heated under reflux for 1 h, since we find that this treatment gives clean reactions by converting the 3-chlorodithiolium salt intermediates (e.g., **13**) into dithiole-3-ones. To our initial surprise, all four starting materials **1a**−**d** gave exactly the same product **2**, as yellow crystals mp 175−177 °C (13−25%) after chromatography (Scheme 1). Mass spectrometry, HRMS, and microanalysis showed **2** to be a monochloro compound $C_8H_4ClNO_2S_5$; the ^1H NMR showed two vicinal methylene groups and ^{13}C NMR showed three unsaturated carbon signals consistent with

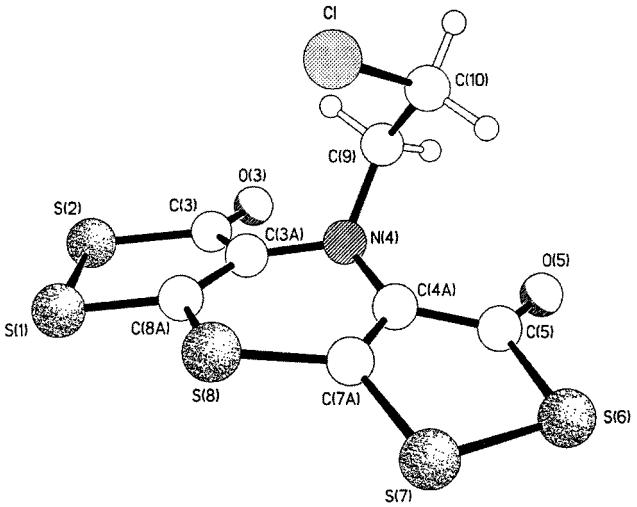


Figure 1. The molecular structure of **2**.

the symmetrical structure in addition to the chloroethyl group, and the IR spectrum showed one carbonyl absorption at 1634 cm^{-1}, all in agreement with the assigned structure 4-(2-chloroethyl)bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*]-[1,4]thiazine-3,5-dione (**2**). The X-ray analysis of **2** shows the molecule to have a scorpion-like conformation (Figure 1), and a pattern of bonding within the fused ring system very similar to that observed for the *N*-ethyl analogue.[8] In both structures the geometry at nitrogen is pyramidal with N(4) lying 0.22 Å out of the plane of its substituents. The principal differences between the two species are a change in the fold angle about the N···S vector in the thiazine ring [25° here compared with 34° for the *N*-ethyl analogue] and in the relative orientations of the C(9)−C(10) bond with respect to the N···S vector in the thiazine ring; the S···N−C−C molecular torsion angles are 39 and −6° in the *N*-chloroethyl and *N*-ethyl species, respectively. A consequence of this torsional relationship in the *N*-chloroethyl compound, and a gauche relationship about the C(9)−C(10) bond, is a directing of the chlorine atom over the center of the thiazine ring, the nonbonded Cl···S(8) distance being 3.85 Å.

An inspection of the packing of the molecules reveals the formation of head-to-tail chains of molecules linked via pairs of O···S interactions (3.10 and 3.19 Å, Figure 2). Adjacent chains in one direction are oriented parallel and coplanar to each other to form sheets. Centrosymmetrically related pairs of sheets are arranged such that the chlorine atoms of molecules within one sheet are directed to lie approximately centrally between the sulfur atoms of the dithiole rings of adjacent chains of the next and *vice versa* thereby stabilizing the sheet structure via Cl···S cross-linking interactions (**a**−**d** in Figure 2).

The geometry of **2** has been optimized using ab initio density functional theory methods,[11] and the results are in agreement with those from the crystallographic analysis. Thus, there seems to be an attractive interaction between the chlorine atom and the thiazine ring that contributes to a crystal structure conformation which is not purely a consequence of the crystal packing.

When the reaction of **1a** (1 equiv) with S_2Cl_2 (1 equiv) was performed in THF without addition of DABCO or

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(11) Rzepa, H.; Conesa, C. *Electronic Conference on Heterocyclic Chemistry ECHET 98*, communication No. 004; for the complete discussion see the web page http://www.ch.ic.ac.uk/ectoc/echet98/pub/004/index.htm.

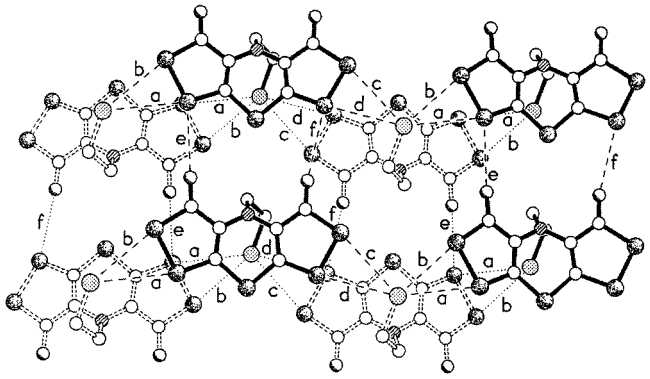
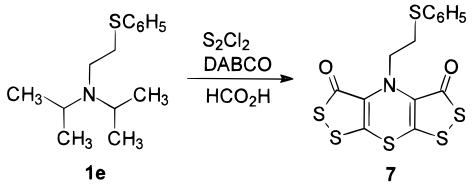


Figure 2. Part of a pair of interlocking sheets of molecules present in the structure of **2** showing the directing of the chlorine atoms in one sheet into the plane of the other and the associated Cl···S and O···S interactions (Å): (a) 3.48; (b) 3.36; (c) 3.53; (d) 3.44; (e) 3.10; (f) 3.19.

Scheme 2



formic acid, the oxothione **3** was obtained as an orange solid, mp 256−258 °C (10%),[12] together with **2** (30%)[12] (Scheme 2). Again the mass spectrum of **3** showed the presence of a chlorine atom and the ^{1}H NMR spectrum two distinctive methylene groups. Desymmetrization of the molecule by the thione group was shown by the appearance of three new signals in the ^{13}C NMR spectrum. IR also confirmed the presence of the thione and ketone groups. Thus the unsymmetrical structure 4-(2-chloroethyl)-3-oxobis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-5-thione (**3**) was fully supported by all its spectroscopic properties. Furthermore, the reaction can be performed without the presence of oxygen donors by quenching the 3-chlorodithiolium salts with an additional base. Thus, **1a** (1 equiv) was treated with S_2Cl_2 (10 equiv), DABCO (5 equiv), and tetramethylammonium chloride (30 mg) as a source of chloride anion, in chloroform for 3 days at room temperature. Triethylamine (13 equiv) was then added and the mixture stirred at room temperature for an additional 3 h. By this extremely mild method, the dithione **4** was obtained as a dark red solid, mp 229−230 °C (14%). The new symmetrical structure 4-(2-chloroethyl)bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5-dithione (**4**) was fully supported by all its spectroscopic properties.

In these reactions the chloroethylamine **1a**, the mercaptoethylamine **1b**, the disulfide **1c**, and the hydroxyethylamine **1d** have reacted with S_2Cl_2 in the same way as Hünig's base itself, without detectable diversion of the reaction pathway, but with the additional conversion at some stage of the thiol, disulfide, and hydroxy groups into the corresponding chloro compound. This last transformation is surprisingly rare for sulfur derivatives, but has been achieved with sulfuryl chloride, followed by treatment with triphenylphosphine.[13]

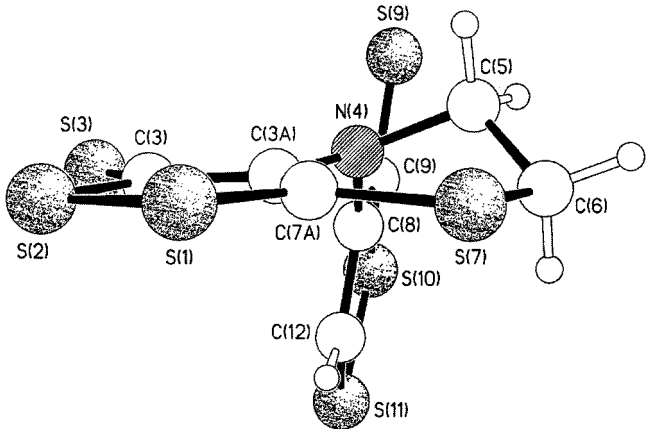


Figure 3. The molecular structure of **5** showing the near-orthogonal relationship between the two dithiole rings and the "sofa" conformation adopted by the thiazine ring.

These results suggest that S_2Cl_2 reacted with the sulfur groups faster than with isopropyl; otherwise the nucleophilic mercapto or hydroxy groups would probably have reacted with some intermediate on the way to the bisdithiolothiazine ring system. We therefore decided to try to regenerate a thiol derivative from the chloro compound by addition of a sulfur nucleophile at a late stage in the reaction. Treatment of the 2-chloroethylamine **1a** (1 equiv) and S_2Cl_2 (1 equiv) in THF for 3 days at room temperature was followed by addition of phosphorus pentasulfide (P_4S_{10}, 0.3 mol) with heating under reflux for 5.5 h. Chromatography gave a new compound **5**, $C_8H_5NS_7$, as shiny orange needles, mp 240−241 °C (40%)[12] (Scheme 1). Treatment of the 2-hydroxyethylamine **1d** in the same conditions gave also **5**, though in much lower yield (7%). This compound **5** did not contain chlorine though two different methylene groups were still present, together with an aromatic methine group, in the ^{1}H and ^{13}C NMR spectra. The IR spectrum showed the presence of thiocarbonyl but not a carbonyl group. The presence of an aromatic proton indicated that the fully fused tricyclic system of **2**−**4** had not been reached, and suggested the presence of a 1,2-dithiole with one ring hydrogen. The lack of either chlorine or mercapto groups bonded to methylene indicated that the ethyl group could be involved in a new ring. The structure 5,6-dihydro-4-(3-thiono[1,2]dithiol-4-yl)[1,2]dithiolo[3,4-*b*][1,4]thiazine-3-thione (**5**) was established by X-ray crystallography. Compound **5** was found to have the partially saturated structure illustrated in Figure 3. The thiazine ring has a "sofa" conformation with C(5) lying 0.7 Å out of the plane of the remaining five atoms (which are coplanar to within 0.07 Å). The geometry at nitrogen is pyramidal, N(4) being 0.28 Å out of the plane of its substituents. The two dithiole rings are oriented approximately orthogonally (ca. 80°) thus minimizing interactions between them. A comparison of the pattern of bonding in these two rings shows that the C(3A)−C(7A) fusion between one of them and the thiazine ring results only in changes in the bond lengths of this bond [1.371(4) Å] and its immediately adjacent neighbor C(7A)−S(1) [1.729(3) Å]

(12) In the absence of DABCO, yields are calculated on the basis of 15 mol of amine **1a** (or **1d**) giving 1 mol of product and 14 mol of amine **1a** (or **1d**) hydrochloride.

(13) Still, I. W. J.; Kutney, G. W.; McLean, D. *J. Org. Chem.* **1982**, *47*, 560.

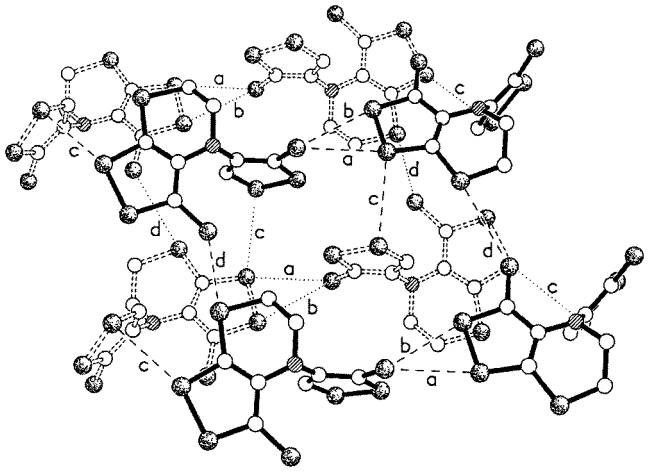


Figure 4. Part of two overlapping sheets of molecules of **5** showing the *intra* and *inter*sheet S···S interactions. The S···S distances (Å) are (a) 3.31; (b) 3.45; (c) 3.52; (d) 3.55.

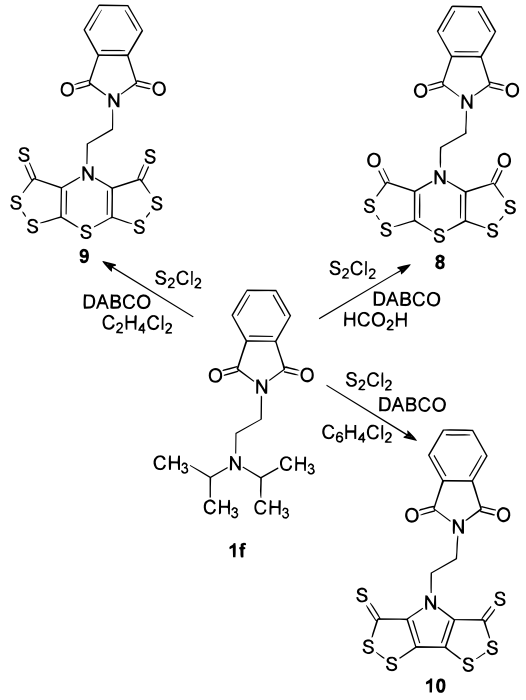
compared to those in the pendant ring system [1.348(4) and 1.705(3) Å for C(8)−C(12) and C(12)−S(11) respectively] which exhibit a higher degree of multiple bond order.

The molecules pack to form sheets which are dominated by short S···S contacts [**a**, **b**, and **d** in Figure 4], the S···S distances ranging between 3.31 and 3.55 Å. Adjacent sheets are offset such that the pendant dithiole rings within one sheet insert into cavities formed between groups of four molecules in a neighboring sheet, the superstructure being stabilized via an additional S···S interaction [**c** in Figure 4] of 3.52 Å. These pendant dithiole rings, although being oriented parallel to each other, are offset, thereby precluding any $\pi\cdots\pi$ interactions between them.

The reaction of 2-chloroethylamine **1a**, S_2Cl_2 and P_2S_5, performed in the presence of DABCO, gave no stable products. Dehydrogenation of **5** to the fully unsaturated 1,4-thiazine ring system by reaction with DDQ was unsuccessful, giving only baseline material on TLC. This was in contrast with the inertness of compound **2**, in which all attempts to displace the chlorine atom with bases or iodide were unsuccessful. Treatment of **2** with diisopropylamine for 7 h, or with sodium diisopropylamide in diisopropylamine for 0.5 h, or with potassium iodide in acetone for 5 h, gave unchanged **2**. Compound **2** was also recovered after stirring with thiourea and sodium hydroxide in water for 3 days, and it did not react with phosphorus pentasulfide or Lawesson's reagent in refluxing THF for 50 h. On the other hand, compound **2** underwent thermal sulfur extrusion by refluxing in chorobenzene for 7 days, affording quantitatively 4-(2-chloroethyl)bis[1,2]dithiolo[4,3-*b*:3′,4′-*d*]pyrrole-3,5-dione (**6**), yellow crystals, mp 245−247 °C, fully characterized by spectroscopy. This slow sulfur extrusion from **2** contrasts with the fast sulfur extrusion from the *N*-ethyl analogue which is complete in 3 h in refluxing xylene.[8] This is probably due to the destabilization of the key reaction intermediate, which requires electron release from the nitrogen atom,[8] by the inductive effect of the chlorine atom.

Because of the inertness of the chlorine atom in the primary alkyl chloride **2**, in reactions with usual nucleophiles, we tried to obtain ethyl-substituted derivatives of the tricyclic 1,4-thiazines by introducing suitable

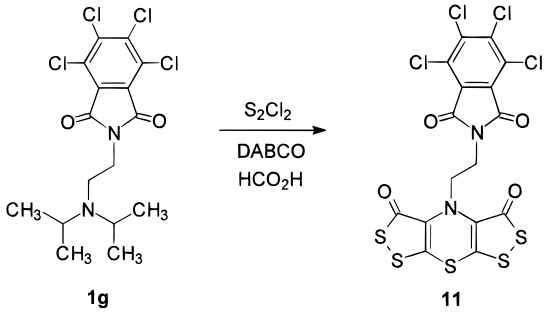
Scheme 3



groups into the starting material. Thus, reaction of *N*-(2-phenylthioethyl)diisopropylamine **1e** (1 equiv), obtained from **1a** and lithium thiophenoxide, with S_2Cl_2 (10 equiv) and DABCO (6 equiv), in 1,2-dichloroethane for 3 days at room temperature and then addition of formic acid (20 equiv) and heating the mixture for 45 min afforded compound **7** as an orange solid, mp 148−149 °C (17%) (Scheme 2). Mass spectrometry and microanalysis showed **7** to be $C_{14}H_9NO_2S_6$, and ^{1}H and ^{13}C NMR spectra showed a phenyl ring and two vicinal methylene groups, supporting the presence of the intact phenylthioethyl group in a bisdithiolothiazine structure, and the carbonyl groups were confirmed by IR, all in agreement with the assigned structure 4-(2-phenylthioethyl)bis[1,2]dithiolo-[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5-dione (**7**). The phenyl ring was not chlorinated by S_2Cl_2. Furthermore, treatment of *N*-(2-diisopropylaminoethyl)phthalimide[14] (**1f**) (1 equiv), readily obtained from **1a** and potassium phthalimide in dimethylformamide, with S_2Cl_2 (10 equiv) and DABCO (10 equiv) in chloroform for 3 d at room temperature and then addition of formic acid (20 equiv) and heating the mixture under reflux for 1.5 h afforded compound **8**, orange crystals, mp 226−228 °C (25%) as the main product (Scheme 3). Mass spectrometry and microanalysis showed **8** to be $C_{16}H_8N_2O_4S_5$, and the ^{1}H NMR spectrum showed the presence of two methylene groups and four aromatic protons, indicating the presence of the phthalimido group in **8** which was assigned the structure 4-(2-phthalimidoethyl)bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-3,5-dione. Compound **8** was not obtainable by the reaction of **2** and potassium phthalimide in DMF, from which only baseline material (TLC) could be observed. Treatment of **1f** (1 equiv) with S_2Cl_2 (9 equiv) and DABCO (9 equiv) in 1,2-dichloroethane for 3 days at room temperature and heating the mixture under reflux for 1 h gave compound **9**, black crystals, mp 245−247 °C (26%) after chromatography, as the main product. All spectro-

(14) (a) Moore, R. *J. Am. Chem. Soc.* **1946**, *68*, 1657. (b) Chiti, S. *Farm. Ed. Sci.* **1958**, *13*, 261 and 276.

Scheme 4



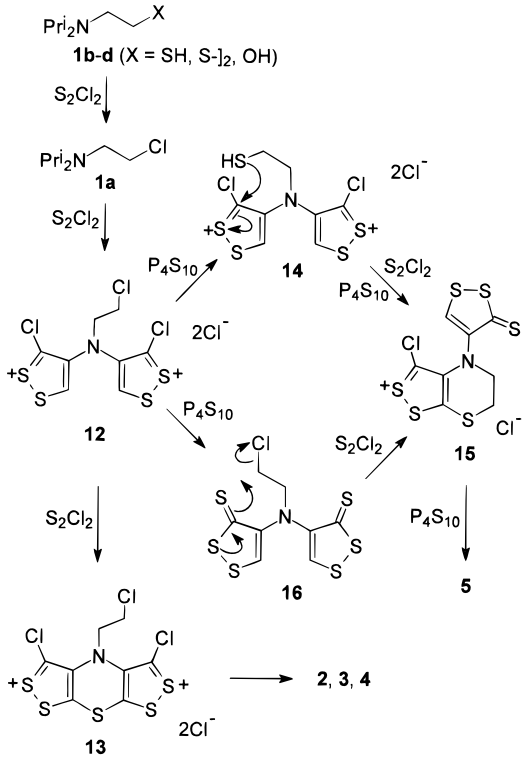
scopic data indicated for this compound **9** the structure corresponding to the dithiono derivative of **8**. In addition, the reaction of **1f** (1 equiv) with S_2Cl_2 (9 equiv) and DABCO (9 equiv) in 1,2-dichlorobenzene for 3 days at room temperature and heating the mixture under reflux for 1.5 h afforded compound **10**, black crystals, mp 291−293 °C as the only product (63%). Mass spectrometry and microanalysis showed **10** to be $C_{16}H_8N_2O_2S_6$ and all spectroscopic data indicated that **10** was the sulfur extrusion product from **9**, the 4-(2-phthalimidoethyl)bis-[1,2]dithiolo[4,3-*b*:3′,4′-*d*]pyrrole-3,5-dithione (**10**). In a similar way, treatment of *N*-(2-diisopropylaminoethyl)-3,4,5,6-tetrachlorophthalimide (**1g**) (1 equiv), readily obtained from **1a** and sodium tetrachlorophthalimide in dimethylformamide, with S_2Cl_2 (10 equiv) and DABCO (5 equiv) in dichloroethane for 3 d at room temperature and then addition of formic acid (20 equiv) and heating the mixture under reflux for 45 min afforded compound **11**, orange crystals, mp 238−240 °C (16%) (Scheme 4) which was fully supported by spectroscopic and analytical data.

In contrast with the straightforward synthesis of compounds **8**−**11**, their inertness and low solubility in common solvents made their chemistry difficult. Thus, all attempts at deprotection of the amino group from phthalimide derivatives **8**−**11** were unsuccessful. For example, refluxing **10** and hydrazine hydrochloride in ethanol for 24 h left **10** unchanged and the same reaction in DMF for 8 h completely decomposed **10**. Refluxing **10** and concentrated hydrochloric or hydrobromic acid in aqueous dimethyl sulfoxide or aqueous chloroform left **10** unchanged. On the other hand, treatment of **11** with hydrazine in refluxing ethanol for 4 h, or with ethylenediamine[15] in refluxing acetonitrile for 5 h, gave only intractable solids. Similar attempts at deprotecting **8** and **9** failed.

Reaction Mechanisms. A plausible mechanism for all the transformations of **1a** (as the actual starting material or as obtained in situ by chlorination of **1b**−**d**) could start by formation of an intermediate disalt **12** (cf. ref 8) that may further react with S_2Cl_2 to form, after extrusion of sulfur, the bis[1,2]dithiolo[1,4]thiazine disalt **13**, which affords the dione **2** by reaction with formic acid or, alternatively, a mixture of dione **2** and oxothione **3** by reaction with sulfur and oxygen donors present in the reaction mixture (Scheme 5). Similarly, disalt **13** gives dithione **4** by quenching with triethylamine. Further extrusion of sulfur from **2** affords **6**. In the presence of phosphorus pentasulfide the disalt **12** could give the intermediate **14** which could then cyclize as shown to give

(15) Debenham, J. S.; Fraser-Reid, B. *J. Org. Chem.* **1996**, *61*, 432.

Scheme 5



the partially saturated thiazine **15**, after further chlorination. Salt **15** converts into the final product **5** by reaction with more phosphorus pentasulfide. The complete reaction scheme is probably quite complex and other pathways can be envisaged. Thus, disalt **12** could react with P_4S_{10} to give the intermediate **16** which may cyclize and be chlorinated to give **15**. In some reactions of **1a** (1 equiv) and S_2Cl_2 (1 equiv) in THF, a green mixture of insoluble salts was filtered from the reaction mixture. By treating this mixture with water or methanol, compound **5** was isolated in very low yield (2−6%) after column chromatography, showing that the conversion of **1a** into **5** is a minor pathway even in the absence of P_4S_{10}. Substitution of the chlorine atom in **1a** by groups that resist chlorination and are poorer leaving groups (such as phenylthio or phthalimido) prevents the pathway to **5** and the reaction gives bis[1,2]dithiolo[1,4]thiazine derivatives (such as **7** and **8**) exclusively.

Conclusions

Commercial *N*-(2-chloroethyl)diisopropylamine, and related compounds, are shown to give some quite complex 1,4-thiazine derivatives, such as **2**−**5**, in one-pot reactions with disulfur dichloride. The products can be varied by changing the reactant ratios and solvents, and by the addition of amines, oxygen donors, or phosphorus pentasulfide. The mild reaction conditions should allow the ready elaboration of these structures to give compounds of potential use as new electronic materials in the 1,2-dithiole series,[16] and in pharmaceutical research.[17]

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Experimental Section

Disulfur dichloride, DABCO, phosphorus pentasulfide, lithium thiophenoxide, potassium phthalimide, and tetrachlorophthalimide were purchased from Aldrich and used without further purification. *N*-(2-Chloroethyl)diisopropylamine hydrochloride (Aldrich) was used as source of free amine. THF was distilled from sodium. 1,2-Dichloroethane and chlorobenzene were distilled from phosphorus pentoxide. Melting points were determined using a Kofler hot-stage apparatus. CH_2 and CH groups were identified by DEPT experiments on representative examples. Column chromatography (MPLC) was carried out on a medium-pressure Gilson liquid chromatography apparatus, with silica gel C60 (Merck). Petroleum ether refers to the fraction bp 40−60 °C.

4-(2-Chloroethyl)bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-3,5-dione (2). Disulfur dichloride (4.0 mL, 50 mmol) was added dropwise to a solution of recently distilled *N*-(2-chloroethyl)diisopropylamine (**1a**) (0.82 g, 5 mmol) [from treatment of its hydrochloride with aqueous sodium hydroxide at 0 °C, and extraction with ice-cold diethyl ether], or (2-diisopropylamino)ethanethiol (**1b**)[10] (0.81 g, 5 mmol), or bis-[2-(diisopropylamino)ethyl]disulfide (**1c**)[10] (0.80 g, 2.5 mmol) or *N*-(2-hydroxyethyl)diisopropylamine (**1d**) (0.73 g, 5 mmol) and DABCO (5.0 g, 45 mmol, for **1a**, and 4.5 g, 40 mmol, for **1b**, **1c**, and **1d**) in 1,2-dichloroethane (100 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C and then for 3 days at room temperature. Formic acid (4 mL, 100 mmol) was then added dropwise at 5 °C and the mixture refluxed for 1 h (for **1a**,**b** and **1d**) and 2 h (for **1c**). The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. MPLC (silica gel Merck 60, petroleum ether to CH_2Cl_2) of the residue afforded **2** as yellow crystals (petroleum ether/CH_2Cl_2) (427 mg, 25%) from **1a** or **1b**, (274 mg, 16%) from **1c**, and (222 mg, 13%) from **1d**; mp 175−177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.73 (t, *J* 5.7, 2H, CH_2), 4.23 (t, *J* 5.7, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 43.43 and 47.22 (2 × CH_2), 136.62 and 146.68 (2 × sp$^2C_{tertiary}$), 182.08 (*C*═O); IR (CCl_4, cm^{-1}) ν_{max} 1666 and 1634 (C═O), 1561, 1522; *m*/*z* (EI, 70 eV) 343 (M^+ + 2, 30), 341 (M^+, 51), 305 (M − 36, 44), 292 (M − 49, 67); HRMS, M^+ = 340.8537 $C_8H_4ClNO_2S_5$ required 340.8534. Anal. Calcd for $C_8H_4ClNO_2S_5$: C, 28.11; H, 1.18; N, 4.10. Found: C, 28.45; H, 0.90; N, 3.92.

Crystal data for 2: $C_8H_4NO_2S_5Cl$, *M* = 341.9, triclinic, $P\bar{1}$ (no. 2), *a* = 7.064(1), *b* = 8.320(1), *c* = 11.427(1) Å, α = 76.77-(1), *β* = 73.45(1), *γ* = 66.53(1)°, *V* = 585.5(1) Å^3, *Z* = 2, D_c = 1.939 g cm^{-3}, *μ*(Mo−Kα) = 12.0 cm^{-1}, *F*(000) = 344. An orange block of dimensions 0.93 × 0.90 × 0.60 mm was used. 11832 Independent reflections were measured at 153 K on a Siemens P4/PC diffractometer with Mo−Kα radiation (*λ* = 0.71073 Å) using *ω*-scans. The structure was solved by direct methods and all of the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 with absorption corrected data (Gaussian, max. and min transmission factors 0.53 and 0.38, respectively) to give R_1 = 0.039, wR_2 = 0.102 for 9303 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 98°$] and 155 parameters; CCDC 126155.

4-(2-Chloroethyl)-3-oxobis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-5-thione (3). Disulfur dichloride (3.3 mL, 40 mmol) was added dropwise to a solution of recently distilled *N*-(2-chloroethyl)diisopropylamine (**1a**) (6.65 g, 40 mmol), in THF (50 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C and then for 3 days at room temperature and then refluxed for 2.5 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. MPLC (petroleum ether to CH_2Cl_2) of the residue afforded compound **3** as orange crystals (petroleum ether/CH_2Cl_2) (96 mg, 10%);[12] mp 256−258 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.71 (t, *J* 5.7, 2H, CH_2), 4.43 (m, br, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 43.19 and 47.66 (2 × CH_2), 137.08, 147.74, 148.42 and 155.75 (4 × sp$^2C_{tertiary}$), 182.18 (*C*═O), 200.90 (*C*═S); IR (CCl_4, cm^{-1}) ν_{max} 1657 and 1637 (C═O), 1552, 1479, 1285 (C═S); *m*/*z* (EI, 70 eV) 359 (M^+ + 2, 21), 357 (M^+, 35), 322 (M − 35, 14), 308 (M − 49, 10), 295 (M − 62, 27); HRMS, M^+ = 356.8387 $C_8H_4ClNOS_6$ required 356.8306. Anal. Calcd for $C_8H_4ClNOS_6$: C, 26.84; H, 1.13; N, 3.91. Found: C, 27.08; H, 0.91; N, 3.81. Compound **2** (277 mg, 30%)[12] was also obtained.

4-(2-Chloroethyl)bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-3,5-dithione (4). Disulfur dichloride (4 mL, 50 mmol) was added dropwise to a solution of recently distilled *N*-(2-chloroethyl)diisopropylamine (**1a**) (0.82 g, 5 mmol), DABCO (2.80 g, 25 mmol), and tetramethylammonium chloride (30 mg) in chloroform (100 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C and then for 3 days at room temperature. Triethylamine (9.1 mL, 65 mmol) was then added and the mixture stirred at room temperature for additional 3 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. MPLC (petroleum ether to a mixture of petroleum ether/CH_2Cl_2 1:1) of the residue afforded compound **4** as a dark red solid (petroleum ether/CH_2Cl_2) (262 mg, 14%); mp 229−230 °C. ^{1}H NMR (400 MHz, pyridine-d_5) δ_H 3.92 (t, *J* 6.1, 2H, CH_2), 4.91 (t, *J* 6.1, 2H, CH_2); ^{13}C NMR (100 MHz, pyridine-d_5) δ_C 43.74 and 48.83 (2 × CH_2), 148.31 and 159.40 (2 × sp$^2C_{tertiary}$), 203.24 (*C*═S); IR (CCl_4, cm^{-1}) ν_{max} 1490, 1452, 1312 (C═S); *m*/*z* (EI, 70 eV) 323 (M − 50, 12). Anal. Calcd for $C_8H_4ClNS_7$: C, 25.69; H, 1.08; N, 3.75. Found: C, 25.64; H, 1.12; N, 3.79.

5,6-Dihydro-4-(3-thiono[1,2]dithiol-4-yl)-[1,2]dithiolo-[3,4-*b*][1,4]thiazine-3-thione (5). Disulfur dichloride (2.86 mL, 35 mmol) was added dropwise to a solution of recently distilled *N*-(2-chloroethyl)diisopropylamine (**1a**) (5.73 g, 35 mmol) or *N*-(2-hydroxyethyl)diisopropylamine (**1d**) (5.65 g, 35 mmol) in THF (50 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C and then for 3 days at room temperature. Phosphorus pentasulfide (4.45 g, 10 mmol) was then added and the mixture refluxed for 5.5 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. MPLC (petroleum ether to CH_2Cl_2) of the residue afforded **5** as orange needles (petroleum ether/CH_2Cl_2) (317 mg, 40%)[12] from **1a** and (56 mg, 7%)[12] from **1d**; mp 240−241 °C. ^{1}H NMR (400 MHz, pyridine-d_5) δ_H 3.01 (t, *J* 4.7, 2H, CH_2), 4.05 (m, br, 2H, CH_2), 7.72 (s, 1H, C═CH); ^{13}C NMR (100 MHz, pyridine-d_5) δ_C 23.13 and 47.31 (2 × CH_2 from DEPT), 142.40 (sp^{2}CH from DEPT), 144.80, 153.25 and 157.20 (3 × sp$^2C_{tertiary}$), 203.60 and 210.80 (2 × *C*═S); IR (CCl_4, cm^{-1}) ν_{max} 1460, 1345 and 1317 (C═S), 1242; *m*/*z* (EI, 70 eV) 339 (M^+, 46), 306 (M − 33, 19), 275 (M − 64, 96); HRMS, M^+ = 338.8466 $C_8H_5NS_7$ required 338.8467. Anal. Calcd for $C_8H_5NS_7$: C, 28.30; H, 1.48; N, 4.13. Found: C, 28.16; H, 1.58; N, 3.95. Crystal data for compound **5** have already been deposited; CCDC 182/736.

4-(2-Chloroethyl)bis[1,2]dithiolo[4,3-*b*:3′,4′-*d*]pyrrole-3,5-dione (6). Compound **2** (100 mg, 0.3 mmol) was heated at reflux in chlorobenzene (60 mL) for 7 days, affording **6** as yellow crystals (petroleum ether/CH_2Cl_2) (90 mg, 99%); mp 245−247 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.78 (t, *J* 5.8, 2H, CH_2), 4.82 (t, *J* 5.8, 2H, CH_2); ^{13}C NMR (100 MHz, pyridine-d_5) δ_C 44.08 and 44.79 (2 × CH_2), 131.95 and 135.99 (2 × sp$^2C_{tertiary}$), 182.35 (C═O); IR (KBr, cm^{-1}) ν_{max} 1639 and 1624 (C═O), 1339; *m*/*z* (EI, 70 eV) 311 (M^+ + 2, 49), 309 (M^+, 100), 273 (M − 36, 27), 260 (M − 49, 72); HRMS, M^+ = 308.8809 $C_8H_4ClNO_2S_4$ required 308.8813. Anal. Calcd. for $C_8H_4ClNO_2S_4$: C, 32.49; H, 1.35; N, 4.74. Found: C, 32.36; H, 1.62; N, 4.56.

4-(2-Phenylthioethyl)bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-3,5-dione (7). Lithium thiophenoxide, 1.0 M solution in THF (12 mL, 12 mmol), was added dropwise to a solution of recently distilled *N*-(2-chloroethyl)diisopropylamine (**1a**) (1.97 g, 12 mmol) in THF (22 mL), and the mixture was stirred for 2 days at room temperature, affording *N*-(2-phenylthioethyl)diisopropylamine (**1e**) as a liquid (2.57 g, 90%), *m*/*z* (EI, 70 eV) 238 (M^+ + 1, 20). Disulfur dichloride (4 mL, 50 mmol) was added dropwise to a solution of *N*-(2-phenylthioethyl)diisopropylamine (**1e**) (1.19 g, 5 mmol), DABCO (3.37 g, 30 mmol), and tetramethylammonium chloride (30 mg) in 1,2-dichloroethane (100 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C and then for 3 days at room temperature. Formic acid (4 mL, 100 mmol) was then added dropwise at 5 °C and the mixture refluxed for 45 min. The reaction mixture was filtered through Celite, and the solvent was removed in

the rotary evaporator. MPLC (petroleum ether to CH_2Cl_2) of the residue afforded **7** as an orange solid (petroleum ether/CH_2Cl_2) (353 mg, 17%); mp 148−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.18 (t, *J* 6.4, 2H, CH_2), 4.04 (t, *J* 6.4, 2H, CH_2), 7.18−7.31 (m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 34.04 and 44.37 (2 × *C*H_2, from DEPT), 126.71, 129.10 and 129.88 (3 × *C*$H_{aromatic}$, from DEPT), 134.82, 136.60 and 146.30 (3 × sp^2*C*$_{tertiary}$), 181.96 (*C*═O); IR (CCl_4, cm^{-1}) ν_{max} 1663 (C═O), 1559; *m*/*z* (EI, 70 eV) 415 (M^+, 10), 305 (M − 110, 10), 278 (M − 137, 11), 273 (M − 142, 20), 77 (100); HRMS, M^+ = 414.8934 $C_{14}H_9NO_2S_6$ requires 414.8958. Anal. Calcd. for $C_{14}H_9NO_2S_6$: C, 40.46; H, 2.18; N, 3.37. Found: C, 40.47; H, 2.07; N, 3.23.

4-(2-Phthalimidoethyl)bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-3,5-dione (8). Disulfur dichloride (5.3 mL, 65 mmol) was added dropwise to a solution of *N*-(2-diisopropylaminoethyl)phthalimide[14] (**1f**) (1.79 g, 6.5 mmol) and DABCO (7.31 g, 65 mmol) in absolute chloroform (100 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C and then for 3 days at room temperature. Formic acid (5.2 mL, 130 mmol) was then added dropwise at 5 °C and the mixture refluxed for 1.5 h. The reaction mixture was filtered through Celite and the solvent was removed in the rotary evaporator. MPLC (petroleum ether to CH_2Cl_2) of the residue afforded **8** as orange crystals (petroleum ether/CH_2Cl_2) (736 mg, 25%); mp 226−228 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.96 (t, *J* 6.1, 2H, CH_2), 4.33 (t, *J* 6.1, 2H, CH_2), 7.74 (m, 2H, Ph), 7.84 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 37.92 and 42.63 (2 × *C*H_2), 123.34 and 134.15 (2 × *C*$H_{aromatic}$), 131.97, 136.30 and 145.85 (3 × sp^2*C*$_{tertiary}$), 168.10 and 181.73 (2 × *C*═O); IR (CCl_4, cm^{-1}) ν_{max} 1772, 1710, and 1624 (C═O), 1559, 1519; *m*/*z* (EI, 70 eV) 452 (M^+, 54), 420 (M − 32, 6), 337 (10), 305 (10), 292 (M − 160, 73), 174 (100); HRMS, M^+ = 451.9093 $C_{16}H_8N_2O_4S_5$ requires 451.9088. Anal. Calcd for $C_{16}H_8N_2O_4S_5$: C, 42.47; H, 1.78; N, 6.19. Found: C, 42.34; H, 1.91; N, 6.26.

4-(2-Phthalimidoethyl)bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-3,5-dithione (9). Disulfur dichloride (2.65 mL, 33 mmol) was added dropwise to a solution of *N*-(2-diisopropylaminoethyl)phthalimide[14] (**1f**) (1 g, 3.65 mmol), DABCO (3.75 g, 33 mmol) in 1,2-dichloroethane (50 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C, then for 3 days at room temperature and then refluxed for 1 h. The reaction mixture was filtered through Celite and the solvent was removed in the rotary evaporator. MPLC (petroleum ether to CH_2Cl_2) of the residue afforded **9**, black crystals (petroleum ether/CH_2Cl_2) (460 mg, 26%); mp 245−247 °C. ^{1}H NMR (400 MHz, pyridine-d_5) δ_H 4.15 (t, *J* 6.1, 2H, CH_2), 5.18 (t, *J* 6.1, 2H, CH_2), 7.55 (m, 2H, Ph), 7.79 (m, 2H, Ph); ^{13}C NMR (100 MHz, pyridine-d_5) δ_C 38.28 and 44.66 (2 × *C*H_2, from DEPT), 123.27 and 134.29 (2 × *C*$H_{aromatic}$, from DEPT), 132.64, 148.20 and 158.38 (3 × sp^2*C*$_{tertiary}$), 168.42 (*C*═O), 203.23 (*C*═S); IR (CCl_4, cm^{-1}) ν_{max} 1768 and 1707 (C═O), 1392, 1306 (C═S); *m*/*z* (EI, 70 eV) 484 (M^+, 8), 452 (M − 32, 55), 420 (M − 64, 37), 174 (100); HRMS, M^+ = 483.8638 $C_{16}H_8N_2O_2S_7$ requires 483.8631. Anal. Calcd for $C_{16}H_8N_2O_2S_7$: C, 39.65; H, 1.66; N, 5.78. Found: C, 40.64; H, 1.84; N, 6.07.

4-(2-Phthalimidoethyl)bis[1,2]dithiolo[4,3-*b*:3′,4′-*d*]pyrrole-3,5-dithione (10). Disulfur dichloride (2.65 mL, 33.1 mmol) was added dropwise to a solution of *N*-(2-diisopropylaminoethyl)phthalimide[14] (**1f**) and DABCO (3.75 g, 33 mmol) in 1,2-dichlorobenzene (50 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C and then for 3 days at room temperature and then refluxed for 1.5 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. MPLC (petroleum ether to CH_2Cl_2) of the residue afforded **10**, black crystals (petroleum ether/CH_2Cl_2) (1.04 g, 63%); mp 291−293 °C. ^{1}H NMR (400 MHz, pyridine-d_5) δ_H 4.37 (t, *J* 4.8, 2H, CH_2), 5.93 (t, *J* 4.8, 2H, CH_2), 7.49 (q, J_{a-b} 5.3, J_{a-c} 3.0, 2H, Ph), 7.76 (q, J_{b-a} 5.3, J_{b-d} 3.0, 2H, Ph); ^{13}C NMR (100 MHz, pyridine-d_5) δ_C 40.34 and 41.58 (2 × *C*H_2, from DEPT), 124.76 and 135.74 (2 × *C*$H_{aromatic}$, from DEPT), 134.16, 139.25 and 147.49 (3 × sp^2*C*$_{tertiary}$), 169.68 (*C*═O), 201.48 (*C*═S); IR (CCl_4, cm^{-1}) ν_{max} 1763 and 1702 (C═O), 1430, 1346, 1275 (C═S); *m*/*z* (EI, 70 eV) 454 (M + 2, 31), 452 (M^+, 100), 419 (M − 33, 18); HRMS, M^+ = 451.8931 $C_{16}H_8N_2O_2S_6$ requires 451.8910. Anal. Calcd for $C_{16}H_8N_2O_2S_6$: C, 42.46; H, 1.78; N, 6.19. Found: C, 42.35; H, 1.84; N, 6.04.

4-[2-(Tetrachlorophthalimido)ethyl]bis[1,2]dithiolo-[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5-dione (11). Sodium tetrachlorophthalimide (3.07 g, 10 mmol) [obtained quantitatively from tetrachlorophthalimide (2.85 g, 10 mmol) and sodium hydride (0.26 g, 11 mmol) stirred in THF (50 mL) for 20 h at room temperature] and *N*-(2-chloroethyl)diisopropylamine (**1a**) (1.64 g, 10 mmol) were stirred in dimethylformamide (5 mL) for 18 h at room temperature. The residue afforded *N*-(2-diisopropylaminoethyl)-3,4,5,6-tetrachlorophthalimide (**1g**) as a colorless solid (CH_2Cl_2) (1.45 g, 35%); mp 92−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.96 (d, 12H, *J* 6.3, 4 × CH_3), 2.65 (t, 2H, *J* 6.9, CH_2), 3.01 (q, 2H, *J* 6.3, 2 × CH), 3.68 (t, 2H, *J* 6.9, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 20.67, 39.55, 42.58, 48.48, 127.69, 129.46, 139.89, 163.59 (*C*═O); IR (CCl_4, cm^{-1}) ν_{max} 2969, 1770 and 1712 (C═O), 1401; *m*/*z* (EI, 70 eV) 415 (7), 413 (16), 411 (15), 312 (92), 310 (89), 142 (100). Disulfur dichloride (2.0 mL, 25 mmol) was added dropwise to a solution of *N*-(2-diisopropylaminoethyl)-3,4,5,6-tetrachlorophthalimide (**1g**) (1.03 g, 2.5 mmol), DABCO (1.40 g, 12.5 mmol) and tetramethylammonium chloride (30 mg) in 1,2-dichloroethane (50 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C, then for 3 days at room temperature. Formic acid (2 mL, 50 mmol) was then added dropwise at 5 °C and the mixture refluxed for 45 min. The reaction mixture was filtered through Celite and the solvent was removed in the rotary evaporator. MPLC (petroleum ether to CH_2Cl_2) of the residue afforded **11** as orange crystals (petroleum ether/CH_2Cl_2) (236 mg, 16%); mp 238−240 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.80 (t, *J* 6.8, 2H, CH_2), 3.92 (t, *J* 6.8, 2H, CH_2); ^{1}H NMR (400 MHz, pyridine-d_5) δ_H 5.62 (t, *J* 6.0, 2H, CH_2), 6.16 (t, *J* 6.0, 2H, CH_2); ^{13}C NMR (100 MHz, pyridine-d_5) δ_C 38.67 and 43.01 (2 × *C*H_2), 128.44, 129.41, 137.72, 139.62 and 148.34 (5 × sp^2*C*$_{tertiary}$), 163.58 and 183.39 (2 × *C*═O); IR (CCl_4, cm^{-1}) ν_{max} 1773, 1717, 1661 and 1630 (C═O), 1521; *m*/*z* (EI, 70 eV) 592 (M^+ + 4, 6), 590 (M^+ + 2, 7), 588 (M^+, 5), 560 (M + 4−32, 10), 558 (M + 2−32, 17), 556 (M − 32, 11), 273 (100). Anal. Calcd for $C_{16}H_4Cl_4N_2O_4S_5$: C, 32.55; H, 0.68; N, 4.75. Found: C, 32.78; H, 0.71; N, 4.79.

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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