Synthesis of Thiadiazole, Dithietane, and Imine Derivatives of the [1,2]Dithiolo[1,4]thiazine Ring System

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We report the synthesis of some new polysulfur−nitrogen heterocyclics by cycloaddition reactions to the thioketo group of readily available tricyclic 1,2-dithiole-3-thiones. Thus treatment of bis-[1,2]dithiolo[1,4]thiazine ketothione **1** with diaryl nitrile imines generated from hydrazonoyl chlorides **2a**−**g** gave [1,3,4]thiadiazolylidenyl[1,2]dithiolo[1,4]thiazines **4a**−**g** in high yield. Compounds **4a**−**f**, bearing the same substituents in both aryl groups, were stable but the analogous **4g**,**h** with a *p*-nitrophenyl group on carbon gave the bis[1,2]dithiolo[1,4]thiazine dione **9**, probably by cycloreversion and hydrolysis during chromatography. Treatment of **1**, the bis[1,2]dithiolopyrrole ketothione **13**, and dithione **12** with ethoxycarbonyl azide **11** gave imines **12** and **15** and bisimine **16**, respectively, by an alternative fragmentation of the initial cycloadduct in which the 1,2-dithiole ring is retained. Reaction of **1** with TosMIC gave the imino-1,3-dithietane **17**.

Introduction

The family of poly-sulfur−nitrogen heterocycles includes highly stable aromatic compounds that display physicochemical properties with relevance in the design of new materials, especially those relating to molecular conductors and magnets, which are currently under intense investigation.[1] The interesting properties of many of these heterocycles has increased the need for rapid syntheses of new, potentially useful poly-sulfur−nitrogen heterocycles. We have recently described new polycyclic dithiole derivatives, bis[1,2]dithiolo[1,4]thiazines,[2] bis-[1,2]dithiolopyrroles,[3] a [1,2]dithiolo[1,4]thiazine,[4] and 1,2-dithiolodisulfides[5] that are easily obtained in one-pot reactions from commercial diisopropylamines or diisopropyl sulfide and disulfur dichloride, S_2Cl_2. The thione derivatives of the bis[1,2]dithiolopyrroles and 1,2-dithiolodisulfides behave as 1,3-dipolar reagents in cycloaddition reactions with dimethyl acetylenedicarboxylate, affording 1,3-dithioles.[3,5] Indeed 1,3-dipolar reactivity of simple 1,2-dithiole-3-thiones generally has been explored quite well (see the reviews in ref 6). The thione group of such compounds can also act as the dipolarophile in 1,3-dipolar cycloadditions but this has been much less investigated. We have shown that ethoxycarbonyl nitrile oxide is a very effective 1,3-dipole for addition to the thione group of compounds such as **1**, the addition being followed by spontaneous cycloreversion to give the corresponding carbonyl compounds in high yield.[2,5] Since such cycloadditions to the thione group of our polycyclic compounds could provide a good route to new derivatives, such as dithiole imines, we have now extended these reactions to other 1,3-dipolar and related reagents.

Results and Discussion

By analogy with the above nitrile oxide cycloadditions, the related 1,3-dipole, diphenyl nitrile imine, obtained from *N*′-phenylbenzohydrazonoyl chloride **2a**, could undergo cycloaddition and cycloreversion to convert the thiocarbonyl group into the *N*-phenylimine. However, it has been shown that addition of diphenyl nitrile imine to the thiocarbonyl group of simple monocyclic 1,2-dithiole-3-thiones is followed by spontaneous opening of the dithiole ring, with the extrusion of sulfur, to give a 1,3,4-thiadiazole as the isolated product.[6] We therefore

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(7) (Heat of formation of **3**: 187.58 kcal/mol, heat of formation of **4**: 167.10 kcal/mol, calculated with MOPAC97 on structures after minimization of energies by PM3 method in MOPAC97).

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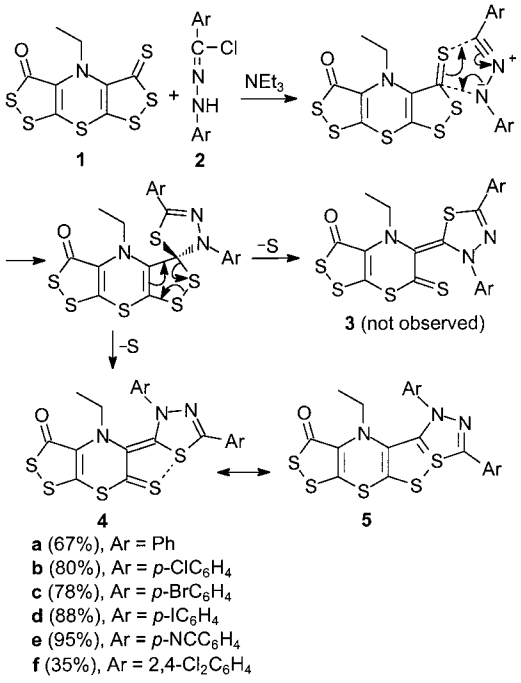
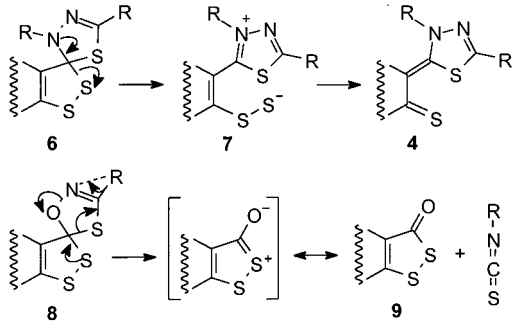
Scheme 1



subjected the bis[1,2]dithiolo[1,4]thiazine ketothione **1**[2] (1 equiv) to reaction with **2a** (2.5 equiv) and triethylamine (3 equiv) in boiling benzene for 1 h. This reaction did not give the *N*-phenylimine or the analogous keto compound **9** (Scheme 2) which could have been formed by hydrolysis of the imine. The product, a red compound mp 160−161 °C (67%) proved to be the 1,3,4-thiadiazole **4a** analogous to that formed from monocyclic 1,2-dithiole-3-thiones.[6] The molecular ion of **4a** corresponded to **1** plus the diphenyl nitrile imine from **2a** minus one sulfur atom, and this was confirmed by HRMS and microanalysis. Its ^{13}C NMR spectrum showed a thiocarbonyl group at an unusually low frequency (δ 185) and a carbonyl group (δ 182) (confirmed by IR spectroscopy), 13 unsaturated carbon signals (two monosubstituted phenyl rings and 5 additional sp^2-tertiary carbon atoms), and two alkyl signals. Its ^{1}H NMR spectrum showed 10 aromatic protons, the methyl group, and two diastereotopic methylenic protons (two sextets), indicating the presence of conformers. A rational mechanism of cycloaddition and sulfur extrusion[6] could afford two different geometrical isomers for the final product, **3a** and **4a**, but we obtained only the latter (Scheme 1). Minimization of energies of **3a** and **4a** by PM3 calculations showed **4a** to have a heat of formation 20 kcal/mol lower than for **3a**,[7] and an attractive interaction, shown by the calculation, between the thione sulfur and the 1,3,4-thiadiazole sulfur atom (**4a** ↔ **5a**). The increased stability of **4a** over **3a** is probably due to this interaction which brings the sulfur atoms closer than the sum of their van der Waals radii. On the other hand, isomer **3** can only exist in a very distorted minimized conformation due to steric hindrance between the thione and the *N*-phenyl ring. Assignment of structure **4a** to the isolated product is supported by the ^{13}C NMR data and was confirmed by comparison with its dibromo derivative **4c** whose structure was proved by X-ray crystallography (see below). In the same way, the reaction of nitrile imines with other aryl groups afforded the corresponding, highly colored products **4b**−**f** (35−95%) (Scheme 1). It is interesting to note that in the

Scheme 2



reaction of the fused 1,2-dithiole-3-thione **1** with diarylnitrile imines the 1,3,4-thiadiazoles **4** are formed, mostly in high yield, with no sign of replacement of the thione by an arylimine to give **10**, while with the nitrile oxide the thione is replaced in high yield by carbonyl, with no sign of 1,3,5-oxathiazole analogous to the 1,3,4-thiadiazoles **4**. Presumably both reactions start by 1,3-dipolar cycloaddition to the thione group to give the (partial) structures **6** and **8** (Scheme 2). In the nitrile imine intermediate **6**, electron release from the saturated nitrogen heteroatom would assist opening of the dithiole ring to give the aromatic thiadiazolium intermediate **7** and hence, on loss of sulfur, the observed product **4**. In the nitrile oxide intermediate **8** the weaker electron release from oxygen will disfavor this process (and formation of the less stable oxathiazolium ring), and a lower energy pathway is fragmentation of the oxathiazole ring (arrows in **8**) to give the dithiole-3-one **9** and isothiocyanate (Scheme 2). In the cycloaddition of nitrile oxides to simple thioketones, the analogous oxathiazoles are more stable and require heating (90−150 °C) to give the ketone and isothiocyanate.[8] Electron release from both 1,2-dithiole sulfur atoms with the formation of an aromatic 1,2-dithiolium ring would account for the spontaneous fragmentation of the spiro intermediate **8**.

All the above diaryl nitrile imine products **4a**−**f** (Scheme 1), bearing the same substituents in each aryl group, are stable and were readily isolated and purified. In contrast, products **4g** and **4h**, obtained from nitrile imines bearing different substituents in the aryl groups, were not stable and reacted during workup with silica in the column chromatography, giving increasing amounts of [1,2]dithiolo[1,4]thiazine dione **9**[2] (Scheme 2) when they were repeatedly passed through silica, making impossible the isolation of pure **4g**,**h**. Deactivated alumina or florisil gave similar results. The structure **9** was confirmed by direct comparison with a pure sample obtained from Hünig's base.[2b] The most plausible way to obtain **9** from **4g**,**h** is the cycloreversion of **4g**,**h** possibly catalyzed by silica, to give first the imines **10g**,**h** which were not isolated but subsequently hydrolyzed by moisture to give **9**. These reactions are probably much faster for the *p*-nitrophenyl imines **4g**,**h** than for imines **4a**−**f**. In support of this mechanism, benzonitrile was isolated from the column chromatography in the attempted preparation of **4f**. Benzonitrile structure was proved by gas chromatography−mass spectrometry and confirmed by comparison with the mass spectrum from the library (94% coincidence).

The structure of compound **4c** was confirmed by single-crystal X-ray diffraction (Figure 1), showing a distance

(8) Huisgen, R.; Mack, W.; Anneser, E. *Angew Chem.* **1961**, *73*, 656.

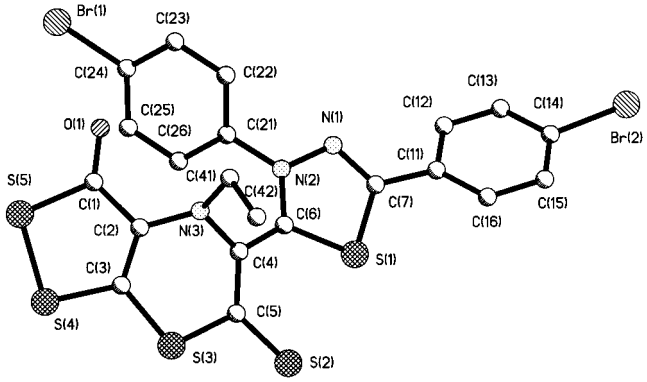


Figure 1. The molecular structure of **4c**.

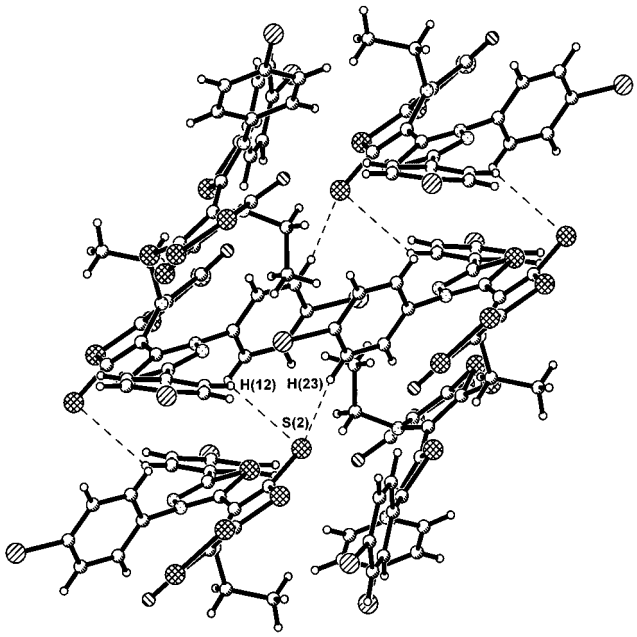


Figure 2. A view of the packing in the crystal of **4c**.

between the thiocarbonyl sulfur S(2) and the thiadiazole sulfur S(1) of 2.965(1) Å that confirmed the predicted sulfur−sulfur interaction and the *E*-geometry of the exocyclic double bond. A view of the packing in the crystal is presented in Figure 2. The most relevant intermolecular contacts are between S(2) and hydrogen atoms of two different adjacent molecules in the direction of the *c* axis. The distances S(2)···H(12) of 2.921(1) Å and S(2)···H(23) of 2.929(1) Å are only slightly shorter than the sum of the van der Waals radii (3.00[9] to 3.25 Å[10]). This creates a three-dimensional network across the crystal. Other weak contacts are S(2)···H(41B) 2.997(1) and Br(2)··· H(25) 2.889(1) Å. Therefore, the observed packing may result from a sum of several weak electrostatic contacts.

The ^{1}H NMR spectrum of compound **4f** showed a complex pattern of signals for the CH_2 group, consisting of four groups of six signals (every group of six signals consisting of two quartets), evidencing the existence of four diastereoisomers. Two diastereoisomers come from the slow interconversion of the *N*-ethyl group and the other two, called atropisomers,[11] from restriction in the

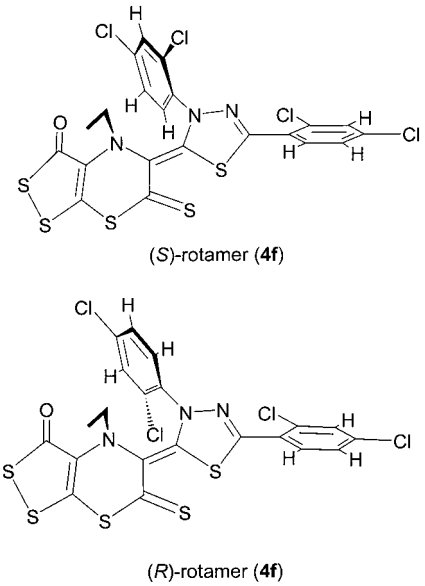
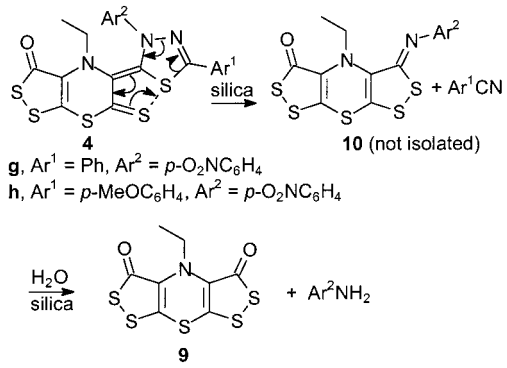


Figure 3.

Scheme 3



rotation of the *N*-(2,4-dichlorophenyl) group. The heat of formation of the (*S*)-atropisomer around the *N*-(2,4-dichlorophenyl) group is lower (0.53 kcal/mol, calculated by PM3 methods on minimized structures) than for the (*R*)-atropisomer (Figure 3), indicating that formation of the (*S*)-atropisomer is more favored than for the (*R*)-atropisomer, thus giving unequal integrals of CH_2 signals in the ^{1}H NMR spectrum of **4f**.

Ethoxycarbonyl azide **11** has been shown to react with simple 1,2-dithiole-3-thiones to afford the corresponding 3-ethoxycarbonylimines.[12] In view of the instability of the *p*-nitrophenylimines **10g**,**h** (Scheme 3) proposed above, we questioned whether the analogous ethoxycarbonylimine **12** (Scheme 4), formed from the thione **1**, would be isolable or readily hydrolyzed on chromatography. We therefore treated thione **1** (1 equiv) and ethoxycarbonyl azide **11** (2.5 equiv) in boiling benzene for 12 h and obtained imine **12** as a stable orange solid, mp 191−192 °C (36%), which was characterized by spectroscopy. However other alkoxycarbonyl azides [(2-chloroethoxy)-carbonyl azide, (+)-menthyloxycarbonyl azide, 4-azidocarbonyloxy-2,2,6,6-tetramethylpiperidinyloxy (4-azidocarbonyloxy-TEMPO)] afforded unstable imines that decomposed during purification or storage; commercial 1-azidoadamantane or 4-carboxybenzenesulfonazide did not react with **1**. The reaction with ethoxycarbonyl azide

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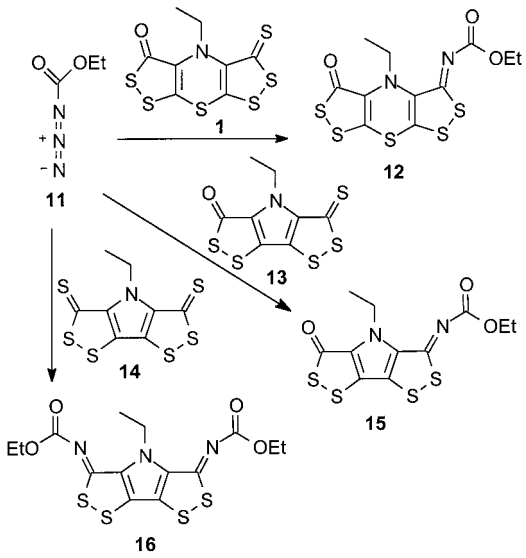
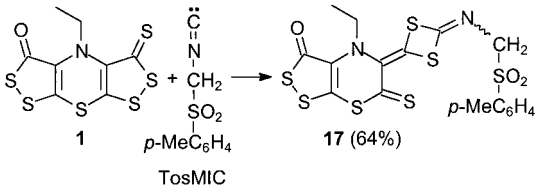
Scheme 4



Scheme 5



11 was successfully applied to bis[1,2]dithiolopyrrole ketothione **13**[3] and dithione **14**,[3] affording respectively the corresponding monoimine **15**, yellow solid, mp 123−124 °C (67%), and diimine **16**, yellow solid, mp 145−146 °C (94%), characterized by spectroscopy and microanalysis (Scheme 4). A reasonable mechanism for the thione to imine conversion is 1,3-dipolar cycloaddition of the azide group to the thione and loss of N_2 to give a thiaziridine ring from which the extrusion of sulfur to give the imine is favored by electron release from the dithiole ring sulfur atoms.

The reaction of bis[1,2]dithiolopyrrole ketothione **13** with nitrile imines **2a** and **2g**,**h** afforded only complex mixtures, products of which were not stable to column chromatography. Nitrogen nucleophiles (arylhydrazines, alkyl- and arylamines, ammonia) either do not react with the dithiolothiazine and dithiolopyrrole derivatives **1**, **13**, and **14**, or give decomposition products, so cycloaddition reactions are a valuable way to modify these structures. We therefore looked for other nitrogen-containing reagents. Diaryldiazomethanes (aryl = C_6H_5, *p*-ClC_6H_4, *p*-$MeOC_6H_4$) gave complex mixtures in their reactions with **1**, and dichloroketene did not react with **1**. Isocyanides take part in a range of interesting addition reactions,[13] although their reactions with [1,2]dithiolethiones are not known. The reaction of equimolecular amounts of **1** and commercial *p*-toluenesulfonylmethyl isocyanide (TosMIC) in benzene at room temperature for 4 h afforded a new compound tentatively assigned structure **17**, a yellow solid, mp 93−95 °C (64%) (Scheme 5), whose microanalysis showed a molecular formula that was the sum of **1** plus TosMIC. The MS of **17** showed peaks at *m*/*z* 323, which corresponded to compound **1** (from HRMS) probably formed in the MS chamber by cycloreversion of **17**, and at *m*/*z* 155 (the *p*-toluenesulfonyl fragment). The ^{1}H NMR of **17** showed four aromatic protons of a *para*-disubstituted phenyl ring, two distinct methylene groups, and two distinct methyl groups. All signals corresponding to the TosMIC part of the molecule appeared doubled with smaller signals, indicating an unequal mixture of geometric imine isomers. This was confirmed by the ^{13}C NMR of **17** that showed a C=S (δ 206) and a C=O (δ 185) group (confirmed by IR), seven sp^2-tertiary carbon atoms, two CH aromatic signals, and four alkyl signals. One of the signals, the CH_2, appeared doubled in the ^{1}H/^{13}C NMR, indicating the presence of geometric imine isomers. The spectroscopic data, and especially cycloreversion of this compound to **1** in the mass spectrometer, suggest the imino-1,3-dithietane structure **17**. To prove this structure we performed the reaction of the bisdithiolothiazinedione **9** with excess TosMIC in refluxing benzene for several hours, monitoring the reaction by TLC. We did not get any reaction product, but only extrusion of sulfur from the starting material, proving that there is no insertion of the isonitrile into one S−S bond.

Conclusion

After 40 years of extensive exploitation, 1,3-dipolar cycloadditions still continue to be very versatile in heterocyclic synthesis, often giving systems that are difficult to obtain by other routes. We have extended this further by cycloaddition of nitrile imines and ethoxycarbonyl azide to the thioketo group of readily available 1,2-dithiole-3-thiones. Nitrile imines give [1,3,4]thiadiazolylidenyl[1,2]dithiolo[1,4]thiazines with opening of the dithiole ring. The azide gives ethoxycarbonyl imines with the dithiole ring retained.

Experimental Section

Bis[1,2]dithiolo[1,4]thiazine ketothione **1**,[2] bis[1,2]dithiolopyrrole ketothione **13**,[2b,3] and dithione **12**[2b,3] were prepared as described. *N*′-Aryl-substituted-benzohydrazonoyl chlorides **2a**−**f** were prepared following known methods.[14] Triethylamine, ethoxycarbonyl azide **11**, and TosMIC were purchased from Aldrich and used without further purification. Benzene was distilled from phosphorus pentoxide. Melting points were determined using a Kofler hot-stage apparatus. Column chromatography 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.

Reactions of Diphenyl Nitrile Imines with [1,2]Dithiolethiones 1. General Procedure. *N*′-Aryl-substituted-benzohydrazonoyl chloride **2a**−**f** (0.70 mmol) and triethylamine (0.12 mL, 0.8 mmol) were added to a solution of **1** (90 mg, 0.28 mmol) in benzene (10 mL). The resulting solution was stirred under reflux for 35 min to 1 h. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by MPLC (Silica gel Merck 60, petroleum ether to CH_2Cl_2) to give the corresponding product.

(*E*)-4-Ethyl-3-oxo-5-(3,5-diphenyl[1,3,4]thiadiazol-2-ylidenyl)[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 4a: red solid (CH_2Cl_2) (91 mg, 67%), mp 160−161 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, J = 6.4 Hz, J = 1.3 Hz, 2H, aromatic H), 7.51 (m, 2H, aromatic H), 7.49 (m, 6H, aromatic H), 3.04 (six signals, double quartet, J = 14.4 Hz, J

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= 7.2 Hz, 1H, $^1/_2CH_2$), 2.60 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 1.02 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (*C*=S), 182.3 (*C*=O), 155.0, 153.4, 152.1, 140.4, 131.9 (5 × sp^2 tertiary C), 131.7, 129.7, 129.3, 129.2 (4 × *C*H aromatic), 128.6 (sp^2 tertiary C), 127.4, 123.9 (2 × *C*H aromatic), 121.3 (sp^2 tertiary C), 47.8 (*C*H_2), 12.7 (*C*H_3); IR (KBr, cm^{-1}) ν 1673 (C=O), 1532, 1423, 1352 (C=S), 1129, 949; MS (EI, 70 eV) *m*/*z* 485 (M$^+$, 46), 456 (M − 29, 79), 376 (9), 293 (11), 250 (17), 77 (100); HRMS, M$^+$ = 484.9815 $C_{21}H_{15}N_3OS_5$ requires 484.9819. Anal. Calcd for $C_{21}H_{15}N_3OS_5$: C, 51.93; H, 3.11; N, 8.65. Found: C, 51.97; H, 2.89; N, 8.42.

(*E*)-4-Ethyl-3-oxo-5-{3,5-di(4-chlorophenyl)[1,3,4]thiadiazol-2-ylidenyl}[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 4b: dark red solid (CH_2Cl_2) (124 mg, 80%), mp 229−230 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 6.8 Hz, J = 1.7 Hz, 2H, aromatic H), 7.48 (dd, J = 6.8 Hz, J = 1.7 Hz, 2H, aromatic H), 7.42 (m, 4H, aromatic H), 3.02 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 2.56 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 1.01 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9 (*C*=S), 182.3 (*C*=O), 154.3, 152.3, 151.9, 138.6, 138.0, 135.6, 131.6 (7 × sp^2 tertiary C), 129.6, 129.3, 128.5 (3 × *C*H aromatic, from DEPT), 127.0 (sp^2 tertiary C), 125.0 (*C*H aromatic, from DEPT), 121.3 (sp^2 tertiary C), 48.0 (*C*H_2, from DEPT), 12.5 (*C*H_3, from DEPT); IR (KBr, cm^{-1}) ν 1638 (C=O), 1541, 1487, 1363 (C=S), 1089; MS (EI, 70 eV) *m*/*z* 557 (M$^+$ + 4, 14), 555 (M$^+$ + 2, 43), 553 (M$^+$, 46), 528 (M + 4 − 29, 30), 526 (M + 2 − 29, 93), 524 (M − 29, 100), 410 (31), 274 (21), 137 (63); HRMS, M$^+$ = 552.9047 $C_{21}H_{13}Cl_2N_3OS_5$ requires 552.9039.

(*E*)-4-Ethyl-3-oxo-5-{3,5-di(4-bromophenyl)[1,3,4]thiadiazol-2-ylidenyl}[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 4c: black prisms with metallic luster (CH_2Cl_2) (142 mg, 79%), mp 251−252 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 6.8 Hz, J = 1.9 Hz, 2H, aromatic H), 7.64 (dd, J = 6.8 Hz, J = 1.9 Hz, 2H, aromatic H), 7.58 (d, J = 8.4 Hz, 2H, aromatic H), 7.33 (d, J = 8.4 Hz, 2H, aromatic H), 3.02 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2$-CH_2), 2.56 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 1.01 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1 (*C*=S), 182.3 (*C*=O), 154.1, 152.2, 152.0, 139.1 (4 × sp^2 tertiary C), 132.6, 132.3 (2 × *C*H aromatic, from DEPT), 131.7 (sp^2 tertiary C), 128.6 (*C*H aromatic, from DEPT), 127.5, 126.4 (2 × sp^2 tertiary C), 125.3 (*C*H aromatic, from DEPT), 123.7, 121.3 (2 × sp^2 tertiary C), 48.0 (*C*H_2, from DEPT), 12.6 (*C*H_3, from DEPT); IR (KBr, cm^{-1}) ν 1644 (C=O), 1542, 1484, 1354 (C=S), 1125; MS (EI, 70 eV) *m*/*z* 645 (M$^+$ + 4, 32), 643 (M$^+$ + 2, 52), 641 (M$^+$, 21), 616 (M + 4−29, 69), 614 (M + 2 − 29, 100), 612 (M − 29, 48), 456 (30), 183 (36); HRMS, M$^+$ + 2 = 642.7993 $C_{21}H_{13}Br^{81}BrN_3OS_5$ requires 642.8008; M$^+$ = 640.8010 $C_{21}H_{13}Br_2N_3OS_5$ requires 640.8029.

Crystal structure determination for compound 4c: Crystals suitable for X-ray study were grown from CH_2Cl_2/petroleum ether solutions. A crystal of dimensions 0.04 × 0.14 × 0.18 mm^3 was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. A full sphere of the reciprocal space was collected up to 2θ = 46.6°. Raw frame data were integrated with the SAINT[15] program. The structure was solved by direct methods with SHELXTL.[16] An empirical absorption correction was applied with the program SADABS.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. All calculations were made with SHELXTL. Final R values were R_1 = 0.0380 for 2356 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1049 (for all 3419 data). Additional material is available from the Cambridge Crystallographic Data Centre, including atomic coordinates, thermal parameters, and a full list of bond lengths and angles (CCDC 165954).

(*E*)-4-Ethyl-3-oxo-5-{3,5-di(4-iodophenyl)[1,3,4]thiadiazol-2-ylidenyl}[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 4d: black prisms (CH_2Cl_2) (182 mg, 88%), mp 235−236 °C (decomp). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.84 (dt, J = 8.6 Hz, J = 1.8 Hz, 2H, aromatic H), 7.77 (d, J = 8.5 Hz, 2H, aromatic H), 7.58 (dt, J = 8.6 Hz, J = 1.8 Hz, 2H, aromatic H), 7.19 (d, J = 8.5 Hz, 2 H, aromatic H), 3.02 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 2.54 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 1.00 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (50 MHz, pyridine-D_5) δ 186.1 (*C*=S), 182.6 (*C*=O), 154.6, 152.5, 152.3, 140.4, 138.6, 138.4, 132.1, 128.8, 128.2, 126.2, 121.4, 99.5 and 96.3 (13C, sp^2 tertiary and aromatic C), 47.9 (*C*H_2), 12.3 (*C*H_3); IR (KBr, cm^{-1}), ν 1647 (C=O), 1540, 1481, 1350 (C=S); EM (FAB$^+$) *m*/*z* 738 (M$^+$ + 1, 36), 737 (M$^+$, 35), 708 (M$^+$ − C_2H_5, 24), 447 (M$^+$ + 1 − $C_8H_5NOS_5$, 92), 369 (100).

(*E*)-4-Ethyl-3-oxo-5-{3,5-di(4-cyanophenyl)[1,3,4]thiadiazol-2-ylidenyl}[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 4e: brown solid (CH_2Cl_2) (142 mg, 95%), mp 174−176 °C (decomp). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.98 (d, J = 9.0 Hz, 2H, aromatic H), 7.79 (d, J = 9.0 Hz, 2 H, aromatic H), 7.75 (d, J = 8.4 Hz, 2H, aromatic H), 7.58 (d, J = 8.4 Hz, 2H, aromatic H), 2.96 (six signals, double quartet, J = 13.5 Hz, J = 6.8 Hz, 1 H, $^1/_2CH_2$), 2.57 (six signals, double quartet, J = 13.5 Hz, J = 6.8 Hz, 1H, $^1/_2CH_2$), 1.01 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (50 MHz, pyridine-d_5) δ 188.2 (*C*=S), 183.1 (*C*=O), 154.2, 151.3, 143.8, 133.9, 133.2, 132.7, 131.9, 129.1, 128.0, 126.4, 125.4, 113.4 and 118.9 (13C, sp^2 tertiary and aromatic C), 114.8 and 113.4 (2 × *C*N), 48.1 (*C*H_2), 12.2 (*C*H_3); IR (KBr, cm^{-1}), ν 2227 (CN), 1654 (C=O), 1602, 1500, 1348 (C=S), 1262, 1098; MS (EI, 70 eV) *m*/*z* 535 (M$^+$, 10), 506 (M$^+$ − C_2H_5, 23), 418 (93), 262 (56); HRMS, M$^+$ = 534.9716 $C_{23}H_{13}N_5OS_5$ requires 534.9724.

(±)(*E*)-4-Ethyl-3-oxo-5-{3,5-di(2,4-dichlorophenyl)[1,3,4]thiadiazol-2-ylidenyl}[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 4f: red solid (CH_2Cl_2) (61 mg, 35%), mp 93−94 °C (decomp). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.89 (d, J = 4.1 Hz, $^1/_2$H, aromatic H), 7.85 (d, J = 4.1 Hz, $^1/_2$ H, aromatic H), 7.69−7.19 (m, 5H, aromatic H), 3.09 (six signals, double quartet, J = 14.2 Hz, J = 7.0 Hz, $^1/_2$H, $^1/_4$CH_2), 2.87 (six signals, double quartet, J = 14.2 Hz, J = 7.0 Hz, $^1/_2$H, $^1/_4$CH_2), 2.90 (six signals, double quartet, J = 14.2 Hz, J = 7.4 Hz, $^1/_2$H, $^1/_4$CH_2), 2.56 (six signals, double quartet, J = 14.2 Hz, J = 7.4 Hz, $^1/_2$H, $^1/_4$CH_2), 1.04 (t, J = 7.0 Hz, 1.5H, $^1/_2$CH_3) 1.03 (t, J = 7.4 Hz, 1.5H, $^1/_2$CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 186.9 (*C*=S), 183.0 (*C*=O), 156.1, 153.1, 149.4, 138.0, 136.5, 133.6, 132.4, 131.8, 131.0, 130.8, 130.3, 128.2, 127.9, 127.6, 126.2, 121.6 and 121.1 (17C, sp^2 tertiary and aromatic C), 49.5 and 49.3 (*C*H_2), 12.4 and 12.0 (*C*H_3); IR (KBr, cm^{-1}), ν 1655 (C=O), 1541, 1508, 1346 (C=S), 1104; MS (EI, 70 eV) *m*/*z* 627 (M$^+$ + 6, 3), 625 (M$^+$ + 4, 8), 623 (M$^+$ + 2, 15), 621 (M$^+$, 9), 596 (20), 594 (33), 592 (21), 175 (14), 173 (67), 171 (100); HRMS, M$^+$ + 2 = 622.8204 $C_{21}H_{11}Cl_3$37ClN_3OS_5 requires 622.8230; M$^+$ = 620.8236 $C_{21}H_{11}$-$Cl_4N_3OS_5$ requires 620.8260.

Reactions of Ethoxycarbonyl Azide 11 and [1,2]-Dithiolethiones 1, 13, and 14. Synthesis of 4-Ethyl-3-oxobis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-5-(*N*-ethoxycarbonyl)imine 12. Ethoxycarbonyl azide **11** (90 mg, 0.78 mmol) was added to a solution of **1** (100 mg, 0.31 mmol) in benzene (10 mL). The resulting solution was stirred under reflux for 12 h. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by MPLC (Silicagel Merck 60, petroleum ether to CH_2Cl_2) to give **12** as an orange solid (CH_2Cl_2−petroleum ether) (42 mg, 36%), mp 191−192 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (quartet, J = 7.2 Hz, 2H, CH_2), 3.97 (quartet, J = 7.2 Hz, 2H, CH_2), 1.38 (t, J = 7.2 Hz, 3H, CH_3), 1.28 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5 (*C*=O), 174.8 (*C*=O), 165.4 (*C*=N), 148.4, 147.7, 139.6, 137.0 (4 × sp^2 tertiary C), 63.6 and 44.2 (2 × *C*H_2), 14.4 and 14.2 (2 × *C*H_3); IR (KBr, cm^{-1}) ν 1653 (C=O), 1614 (C=O), 1519, 1454, 1370, 1299, 1255;

(15) SAINT+. SAX area detector integration program. Version 6.02. Bruker AXS, Inc. Madison, WI, 1999.

(16) G. M. Sheldrick, SHELXTL, an integrated system for solving, refining, and displaying crystal structures from diffraction data. Version 5.1. Bruker AXS, Inc. Madison, WI, 1998.

(17) G. M. Sheldrick, SADABS, Empirical Absorption Correction Program. University of Göttingen: Göttingen, Germany, 1997.

MS (EI, 70 eV) *m*/*z* 378 (M^+, 100), 363 (M − 15, 78), 317 (M − 61, 17), 277 (25), 245 (43); HRMS, $M^+ = 377.9295$ $C_{11}H_{10}N_2O_3S_5$ requires 377.9307. Anal. Calcd for $C_{11}H_{10}N_2O_3S_5$: C, 34.96; H, 2.66. Found: C, 35.12; H, 2.72.

Synthesis of 4-Ethyl-3-oxobis[1,2]dithiolo[4,3-*b*:3′,4′-*d*]-pyrrole-5-(*N*-ethoxycarbonyl)imine 15. Ethoxycarbonyl azide **11** (98 mg, 0.85 mmol) was added to a solution of **13** (100 mg, 0.34 mmol) in toluene (10 mL). The resulting solution was stirred under reflux for 4 h. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by MPLC (Silicagel Merck 60, petroleum ether to CH_2Cl_2) to give **15** as a yellow solid (CH_2Cl_2) (79 mg, 67%), mp 123−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (quartet, $J = 7.1$ Hz, 2H, CH_2), 4.39 (quartet, $J = 7.1$ Hz, 2H, CH_2), 1.43 (t, $J = 7.1$ Hz, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1 (*C*═O), 171.9 (*C*═O), 165.1 (*C*═N), 140.1, 135.3, 130.8, 130.0 (4 × sp^2 tertiary C), 63.7 and 40.6 (2 × *C*H_2), 17.1 and 14.4 (2 × *C*H_3); IR (KBr, cm^{-1}) ν 1654 (C═O), 1277, 1265; MS (EI, 70 eV) *m*/*z* 346 (M^+, 40), 273 (M − 73, 40), 245 (58), 241 (56), 208 (50), 181 (43), 94 (80), 84 (100); HRMS, $M^+ = 345.9574$ $C_{11}H_{10}N_2O_3S_4$ requires 345.9576. Anal. Calcd for $C_{11}H_{10}N_2O_3S_4$: C, 38.14; H, 2.91. Found C, 38.70; H, 2.55.

Synthesis of 4-Ethylbis[1,2]dithiolo[4,3-*b*:3′,4′-*d*]pyrrole-3,5-di(*N*-ethoxycarbonyl)imine 16. Ethoxycarbonyl azide **11** (178 mg, 1.55 mmol) was added to a solution of **14** (95 mg, 0.31 mmol) in toluene (10 mL). The resulting solution was stirred under reflux for 4 h. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by MPLC (Silicagel Merck 60, petroleum ether to CH_2Cl_2) to give **16** as a yellow solid (CH_2Cl_2) (121 mg, 94%), mp 145−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (quartet, $J = 6.9$ Hz, 2H, CH_2), 4.40 (quartet, $J = 7.1$ Hz, 4H, 2 × CH_2), 1.45 (t, $J = 6.9$ Hz, 3H, CH_3), 1.44 (t, $J = 7.1$ Hz, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (*C*═O), 165.2 (*C*═N), 140.5 and 130.9 (sp^2 tertiary C), 63.7 and 41.6 (2 × *C*H_2), 17.1 and 14.5 (2 × *C*H_3); IR (KBr, cm^{-1}) ν 1625 (C═O), 1426, 1433, 1284, 1269; MS (EI, 70 eV) *m*/*z* 417 (M^+, 90), 372 (M − 43, 10), 344 (M − 73, 20), 239 (100), 211 (60), 208 (50), 180 (43); HRMS, $M^+ = 416.9945$ $C_{14}H_{15}N_3O_4S_4$ requires 416.9936. Anal. Calcd for $C_{14}H_{15}N_3O_4S_4$: C, 40.27; H, 3.62; N, 10.06. Found C, 40.38; H, 3.59; N, 9.84.

Reaction of TosMIC with Dithiolethione 1: Synthesis of4-Ethyl-3-oxo-5-{4-[*N*-(*p*-toluenesulfonylmethyl)imino]-[1,3]dithietan-2-ylidenyl)[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 17. TosMIC (59 mg, 0.30 mmol) was added to a solution of **1** (97 mg, 0.30 mmol) in benzene (5 mL). The resulting solution was stirred at room temperature for 4 h. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by MPLC (Silicagel Merck 60, petroleum ether to CH_2Cl_2) to give **15** as a yellow solid (CH_2Cl_2) (100 mg, 64%); mp 93−95 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, $J = 8.1$, 2H, C_6H_5), 7.38 (d, $J = 8.1$, 2H, aromatic H), 4.65/4.72 (2 × s, 2H, CH_2), 3.48 (broad signal, 2H, CH_2), 2.45 (s, 3H, CH_3), 1.18 (t, $J = 6.9$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4 (*C*═S), 184.5 (*C*═O), 156.4, 155.3, 147.2, 145.7, 134.0, 131.65 and 130.4 (7 × sp^2 tertiary C), 130.0 and 129.0 (2 × *C*H aromat), 73.9 and 49.2 (2 × *C*H_2), 21.8 and 13.5 (2 × *C*H_3); IR (KBr, cm^{-1}) ν 2963, 1651 (C═O), 1521, 1324, 1279 (C═S), 1144; MS (EI, 70 eV) *m*/*z* 323 (M − TosMIC, 50), 155 ($TolSO_2$+, 35), 91 (100). Anal. Calcd for $C_{17}H_{14}N_2O_3S_7$: C, 39.36; H, 2.72, N, 5.40. Found: C, 39.66; H, 2.71, N, 5.19.

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

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