polarity) were obtained: recovered 10-ethylphenoxazine (0.18 g, 10%), the ester **3c** [0.30 g, 13%; mp 91 °C after crystallization from hexane; NMR ($CDCl_3$) δ 1.16 (t, 3 H, J = 7.0 Hz, Me), 3.56 (q, 2 H, J = 7.0 Hz, CH_2), 3.89 (s, 3 H, OMe), 6.82–6.98 (m, 6 H, phenox), 7.34 (dd, 1 H, J_o = 7.6 Hz, J_m = 2.6 Hz, H-2], and the ester **2d** (0.50 g, 22%), an oil identical with that synthesized in the manner described below.

10-Ethylphenoxazine-1-carboxylic Acid (3b). A solution of **3c** (0.30 g) in methanol (10 mL) and 5% aqueous sodium hydroxide (5 mL) was heated at reflux temperature for 0.5 h. The reaction mixture was worked up in the manner described above for **2a**. Crystallization of the crude product from dichloromethane–hexane gave **3b** (0.227 g, 80%), mp 149 °C. Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.72; H, 5.15; N, 5.49. This material was identical with a specimen synthesized from phenoxazine-1-carboxylic acid as follows. Phenoxazine-1-carboxylic acid (1.14 g, 5 mmol) was added portionwise to a suspension of sodium hydride (0.528 g, 11 mmol, 50% suspension in mineral oil) in dry DMF (10 mL) at 0 °C. The mixture was then stirred for 2 h at room temperature and cooled to 0 °C, and ethyl iodide (1.72 g, 0.88 mL, 11 mmol) was added thereto. After 18 h at room temperature, the reaction mixture was diluted with water, the product was extracted into ethyl acetate, and the extract was washed with saturated salt solution, dried, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel (120 g) with hexane–ethyl acetate (4:1) to elute the oily ethyl ester of **3b** (1.10 g, 78%). Saponification of this material in the same manner as described above and crystallization of the product from dichloromethane–hexane gave 10-ethylphenoxazine-1-carboxylic acid (82% yield), identical with that described above.

10-Ethylphenoxazine-4-carboxylic Acid (2b). Saponification of **2d** in the manner described above and crystallization of the product from dichloromethane–hexane gave **2b** (85% yield), mp 163–164 °C (lit.[3] mp 163.5–165 °C).

Methyl 10-Ethylphenoxazine-4-carboxylate (2d). Sodium hydride (0.58 g, 1.2 mmol, 50% in mineral oil) was added to a stirred solution of methyl phenoxazine-4-carboxylate (**2c**, 0.241 g, 1 mmol) in dry DMF (5 mL, nitrogen atmosphere). After 0.5 h, ethyl iodide (0.129 g, 1.2 mmol) was added, and after stirring for 10 min the reaction mixture was poured into water. The ester was extracted into ethyl acetate; the extract was washed with water, dried, and evaporated in vacuo. The residue was passed through a short column of silica gel (15 g) with hexane–ethyl acetate (98:2) as the eluting solvent. The ester **2d** (0.255 g, 95% yield), identical with that obtained as described above, was obtained as an oil: IR ($CHCl_3$) 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (t, 3 H, J = 7.5 Hz, CH_3) 3.56 (q, 2 H, J = 7.5 Hz, CH_2), 3.89 (s, 3 H, OMe), 6.40–6.85 (m, 6 H, phenox), 7.07 (dd, 1 H, J_o = 8.0 Hz, J_m = 2.6 Hz, H-3); high-resolution MS calcd for $C_{16}H_{15}NO_3$ 269.1052, found 269.1056.

Acknowledgment. We wish to thank Janice Nelson and Dr. Ken Straub, of the Syntex Analytical Department, for their extra effort on our behalf in obtaining the NMR and mass spectral measurements of the deuterated phenoxazine derivatives.

A New Preparation of 5-(Alkylthio)-1,2-dithiole-3-thiones and a Highly Functionalized 1,3-Dithiole-2-thione

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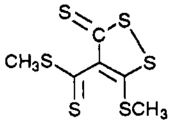
A "one-pot" preparation of the title 1,2-dithiole-3-thiones as well as the preparation and characterization of methyl 5-(methylthio)-2-thioxo-1,3-dithiole-4-dithiocarboxylate (**3**) are described. The X-ray structure determination of an iodine complex of the dithiolodithiole **5** is described in detail. The structure shows that this is a molecular solid with unusual three-dimensional intermolecular sulfur–sulfur "bonding".

The preparation of methyl dithioacetate via methylmagnesium bromide is well known,[1] and its use for the preparation of 1,2-dithiole-3-thione **1** according to Scheme I was reported recently.[2] We, independently, studied this sequence of reactions but with a different base and slightly different conditions. In Scheme I, B: is either sodium methyl dithioacetate or an excess of sodium hydride. If the chemical transformations depicted in Scheme I for methyl dithioacetate could be applied to dimethyl tetrathiomalonate, then heterocycle **2** would be formed.



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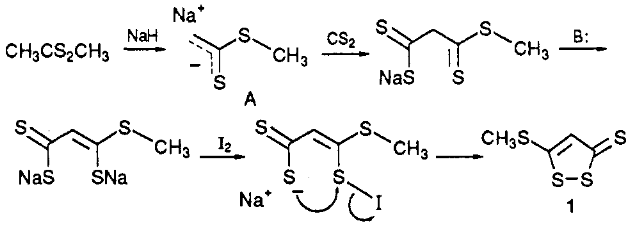
Scheme I



Implicit in Scheme I was the gross, counterintuitive assumption that the ambident anion intermediate (A, Scheme I or B, Scheme II) *was more nucleophilic at its carbon than at its sulfur terminus.* In this publication we show that Scheme I is not only a viable method for the preparation of heterocycle **1**[2] but also for the synthesis of its 5-ethylthio and 5-benzylthio derivatives and that attempts to dithiocarboxylate dimethyl tetrathiomalonate at carbon, followed by iodine oxidation afforded a *1,3-dithiole* (**3**) rather than the expected 1,2-dithiole **2**. We proved the structure of **3** by a reductive alkylation of dithiolo dithiole **5** made by a pyrolytic route and by a pub-

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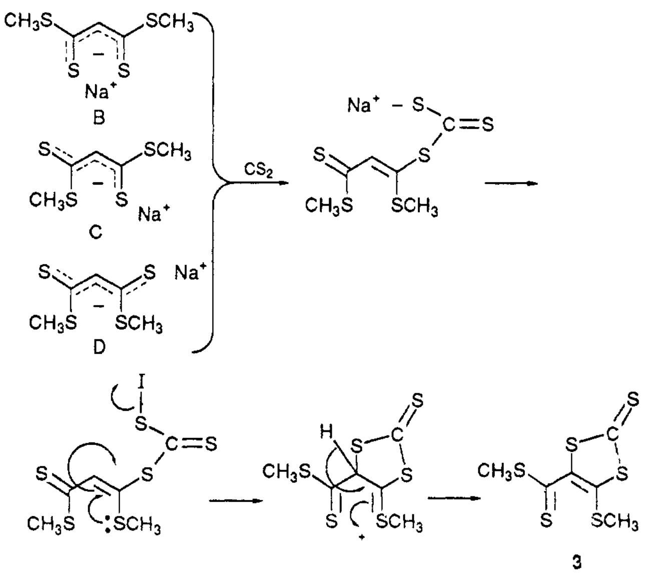
[1] Meijer, J.; Vermeer, P.; Brandsma, L. *Recl, Trav. Chim. Pay-Bas* **1973**, *92*, 601.

[2] Hartke, K.; Hoffmann, R. *Liebigs Ann. Chem.* **1980**, 483. A "thio Claisen condensation" of methyl dithioacetate was also reported: Scheithauer, S.; Mayer, R. *Chem. Ber.* **1967**, *100*, 1413.

Scheme II



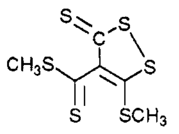
lished procedure. We also report the crystal structure of an iodine complex of **5** which has very short *three-dimensional intermolecular contacts.*

Results and Discussion

Synthesis. Treatment of a solution of methyl dithioacetate and carbon disulfide in THF with sodium hydride, followed by quenching with an iodine solution, afforded the dithiole **1**[3] in ca. 50% yield. It is clear that at least 50% of the negative charge in A was trapped by the carbon disulfide electrophile.[4] It apparently does not matter whether the counterion is sodium or potassium for the attachment of the electrophile to carbon.[2,5]

When ethyl and benzyl dithioacetates were subjected to the reactions outlined in Scheme I, the corresponding 5-(ethylthio)- and 5-(benzylthio)-1,2-dithiole-3-thiones were obtained in moderate yield; yield optimization was not attempted. These results indicate that the preparation of the heterocycles appears to be independent of the alkyl group attached to the dithiocarboxylate sulfur atom.

When dimethyl tetrathiomalonate was subjected to the above-mentioned conditions, a heterocycle with the physical properties expected for **2** was isolated in ca. 30% yield. However, all the usual spectroscopic techniques that were used to determine the structure could not distinguish *unambiguously* between structures **2** and **3**.



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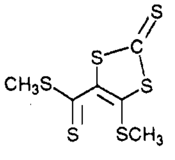

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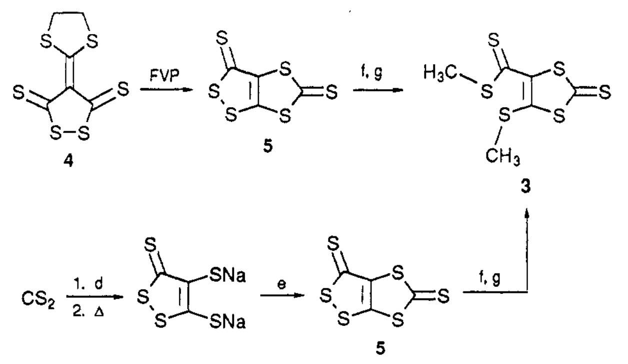
Scheme III^a



^{a}(d) Na/DMF; (e) Cl_2CS; (f) Et_3BHLi/THF; (g) MeI.

Table I. Crystal Data for Compound $5 \bullet I_2$

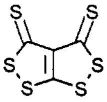
$C_4S_6I_2$	$a = 7.5040\ (18)$ Å
$M_w = 493.8$	$b = 15.5441\ (3)$ Å
space group: $P2_1/n$	$c = 10.0646\ (11)$ Å
$Z = 4$	$\beta = 108.09\ (4)°$
$D_c = 2.91$ g/cm^3	$V = 1115.28$ Å^3

A course of events that could lead to compound **3** is shown in Scheme II.

It appears that in order to form **3**, anion conformer D must be trapped by carbon disulfide at sulfur. Unfortunately the crystals of the product of dithiocarboxylation of dimethyl tetrathiomalonate were not of X-ray diffraction quality, so we resorted to the chemical structure determination outlined in Scheme III.

The preparation and unusual X-ray structural features of the heterocycle **4**[6] employed in the flash vacuum pyrolysis (FVP) reaction in Scheme III was reported recently, as was the preparation of **5** based on a CS_2 reduction–rearrangement.[7] When the properties of the product obtained from reaction of dimethyl tetrathiomalonate and carbon disulfide, followed by iodine were compared with those of **3** obtained in Scheme III, they were found to be identical, indicating that the reaction appears to proceed via steps suggested in Scheme II.

When we had performed the FVP of **4**, and obtained a crystalline product, we assumed (based on simple mechanistic considerations) it was isomer **6**; this, as we show



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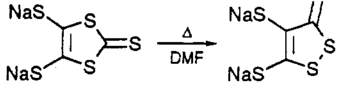
with an X-ray structure determination in this paper, was wrong, and the correct structure of the FVP reaction is actually **5**.[8] Even though the latter had been prepared before, its structure was not fully described[7] and no intuitively satisfactory mechanism for the rearrangement (reaction 1), implicit in the lower half of Scheme III, has been postulated. Unfortunately the crystals of **5** were not



(1)

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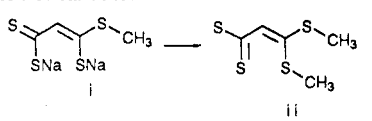
[3] Mouchel, P.; Thuillier, A. *C. R. Acad. Sci. Paris Ser. C* **1967**, *264*, 1552.

[4] Alkylation of the intermediate dianion of Scheme I (also shown as i, below) to form a β,β'-bis(thioalkyl)dithioacrylate (ii) proceeds in 40–50 % yield. Assuming the alkylation to proceed in quantitative yield, this result implies that the ambident anion B is thioacylated at carbon, at least to the extent of ca. 50%.



[5] Thiophenoxide (pK_a 6.52) is 3 orders of magnitude more nucleophilic toward methyl iodide than cyanide (pK_a 9.3): Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319.

[6] Wudl, F.; Srdanov, G.; Rosenau, B.; Wellman, D.; Williams, K.; Cox, S. D. *J. Am. Chem. Soc.* **1988**, *110*, 1316.

[7] Papavassiliou, G. C. *Chem. Scr.* **1985**, *25*, 167.

[8] Scheme IV was published, in part, by us before (Wudl, F.; Srdanov, G.; Rosenau, B.; Wellman, D.; Williams, K.; Cox, S. D.; Yoon, V. *Pure Appl. Chem.* **1987**, *59*, 975) with the assignment of structure **6** for what turned out to be **5**.

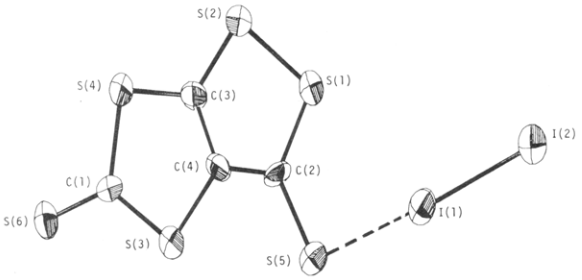


Figure 1. ORTEP drawing of an asymmetric unit of $\mathbf{5}{\cdot}I_2$. The numbers in parentheses refer to Table II.

Table II. Interatomic Distances Corresponding to Figure 1

from	to	distance, nm
I(1)	S(5)	2.719 (6)
I(1)	I(2)	2.841 (2)
S(1)	C(2)	1.728 (19)
S(1)	S(2)	2.062 (8)
S(2)	C(3)	1.693 (19)
S(3)	C(1)	1.729 (19)
S(3)	C(4)	1.750 (18)
S(4)	C(3)	1.717 (20)
S(4)	C(1)	1.771 (19)
S(5)	C(2)	1.703 (18)
S(6)	C(1)	1.610 (20)
C(2)	C(4)	1.387 (26)
C(3)	C(4)	1.381 (25)

Bond Angles (deg) Corresponding to Figure 1

C(2)	S(1)	S(2)	96.2 (9)
C(3)	S(2)	S(1)	94.4 (7)
C(1)	S(3)	C(4)	96.7 (9)
C(3)	S(4)	C(1)	96.2 (9)
S(6)	C(1)	S(3)	126 (1)
S(6)	C(1)	S(4)	120 (1)
S(3)	C(1)	S(4)	114 (1)
C(4)	C(2)	S(5)	124 (1)
C(4)	C(2)	S(1)	113 (1)
S(5)	C(2)	S(1)	122 (1)
C(4)	C(3)	S(2)	117 (1)
C(4)	C(3)	S(4)	117 (1)
S(2)	C(3)	S(4)	126 (1)
C(3)	C(4)	C(2)	119 (2)
C(3)	C(4)	S(3)	116 (1)
C(2)	C(4)	S(3)	125 (1)

suitable for X-ray structure determination, but an iodine complex gave useful crystals. The results presented here indicate that FVP of **4** causes not only loss of ethylene (as we had assumed earlier[8]) but a concomitant rearrangement involving movement of a carbon disulfide moiety from carbon to sulfur;[9] a baffling result since the reverse was observed in the pyrolysis of the reduction product of carbon disulfide (reaction 1).[7,10]

Crystal Structure of $\mathbf{5{\cdot}I_2}$. The X-ray diffraction crystal data on a sample of an iodine complex obtained from **5** in acetonitrile are shown in Table I.

Table III. Intermolecular Distances[a]

Shorter than 4 Å	
I(12)–S(22)^{i}	3.555 (7)
I(12)–I(32)^{ii}	3.781 (3)
S(12)–S(26)^{i}	3.365 (8)
S(12)–S(46)^{iii}	3.434 (8)
S(12)–I(22)^{iv}	3.555 (7)
S(14)–S(46)^{iii}	3.452 (8)
S(16)–S(22)^{iv}	3.365 (8)
S(16)–S(42)^{v}	3.434 (8)
S(16)–S(44)^{v}	3.452 (8)

[a] Key to the Symmetry Operations

(i)	$^1/_2 - x$	$^1/_2 + y$	$^3/_2 - z$
(ii)	$-x$	$1 - y$	$1 - z$
(iii)	$x - {}^1/_2$	$-^1/_2 - y$	$^1/_2 + z$
(iv)	$^1/_2 - x$	$y - {}^1/_2$	$^3/_2 - z$
(v)	$^1/_2 + x$	$-^1/_2 - y$	$-^1/_2 + z$

An ORTEP drawing of the asymmetric unit of $\mathbf{5{\cdot}I_2}$ with intramolecular, interatomic distances and angles is shown in Figure 1 (values for interatomic distances corresponding to this figure are collected in Table II). The sulfur–sulfur distance [S(1)–S(2), 2.062 Å] is the same as for **4**.[6] Carbon–sulfur distances of $\mathbf{5{\cdot}I_2}$ are in the range of 1.693–1.772 Å, showing one short C(3)–S(2) (1.693 Å) bond length, which has also been found previously in another sulfur heterocycle.[11] Both rings are planar with maximum deviation from planarity of 0.026 Å for S(4) and 0.033 Å for S(2). The two rings of the bicycle exhibit a small tilt of 1° relative to each other, and the entire molecule is at a 19° angle with the *bc* plane.

The solid-state packing structure is rather unusual because all molecules are "interconnected" by very short intermolecular S–S as well as S–I contacts (see Table III and Figure 2). These "intermolecular bonds"; for example, S(12)–S(26) and S(16)–S(22) (3.365 Å, .265 Å shorter than the sum of S van der Waals radius) are shorter than those reported (3.39 Å) for the first three-dimensional molecular metal, TTF[Ni(dmit)$_2$]$_2$.[12] Another short "intermolecular bond" is that of thione sulfur S(5) (Figure 1), which has a contact (2.719 Å) with iodine [I(1), Figure 1] that is 1.06 Å shorter than the sum of the van der Waals radii (3.78 Å)! The effect of this interaction is noted also in a significant reduction in the C═S double bond character of the "bonded" thione and an enlargement of the I–I bond from normal (2.68 Å) to 2.841 Å. The I–I distance in this complex is closer to that of triiodide (2.921 Å). While this work was in progress, another short C═S···I–I distance was reported,[13] where the S–I distance ranged from 2.607 to 2.616 Å and the I–I bond length ranged from 2.967 to 2.984 Å.

The X-ray crystal structure of "complex" $5{\cdot}I_2$, shows without doubt that this solid is not a charge-transfer complex but a solid with S–I–I bonds. Thus, even though $\mathbf{5{\cdot}I_2}$ is a shiny, black solid, it is an electrical insulator, as determined by a two-probe conductivity measurement.

Experimental Section

All operations were carried out under inert atmosphere conditions using either argon or pure nitrogen atmospheres. The preparation of ethyl and benzyl dithioacetate followed exactly the same procedure as that for the methyl ester with some exceptions noted below. "Standard workup" means: The aqueous phase was extracted with ether (2×) and the combined organic

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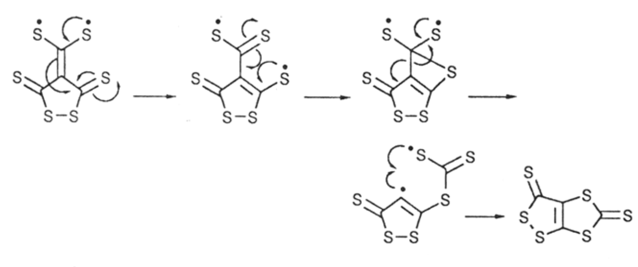
(9) A highly speculative interpretation of this observation which would keep the rearranging CS_2 bound is shown below:



(10) Steimecke, G.; Sieler, H. J.; Kirmse, R.; Ditzseh, E.; Hoyer, E. *Phosphorus Sulfur* **1982**, *12*, 237.

(11) Kimura, M.; Watson, W. H.; Nakayama, J. *J. Org. Chem.* **1980**, *45*, 3719–3721 (supplementary Material).

(12) Bousseau, M.; Valade, L.; Bruniquel, M.-F.; Cassoux, P.; Garbauskas, M.; Interrante, L.; Kasper, J. *Nouv. J. Chim.* **1984**, *8*, 3.

(13) Freeman, F.; Ziller, J. W.; Po, H. N.; Keindl, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 2586.

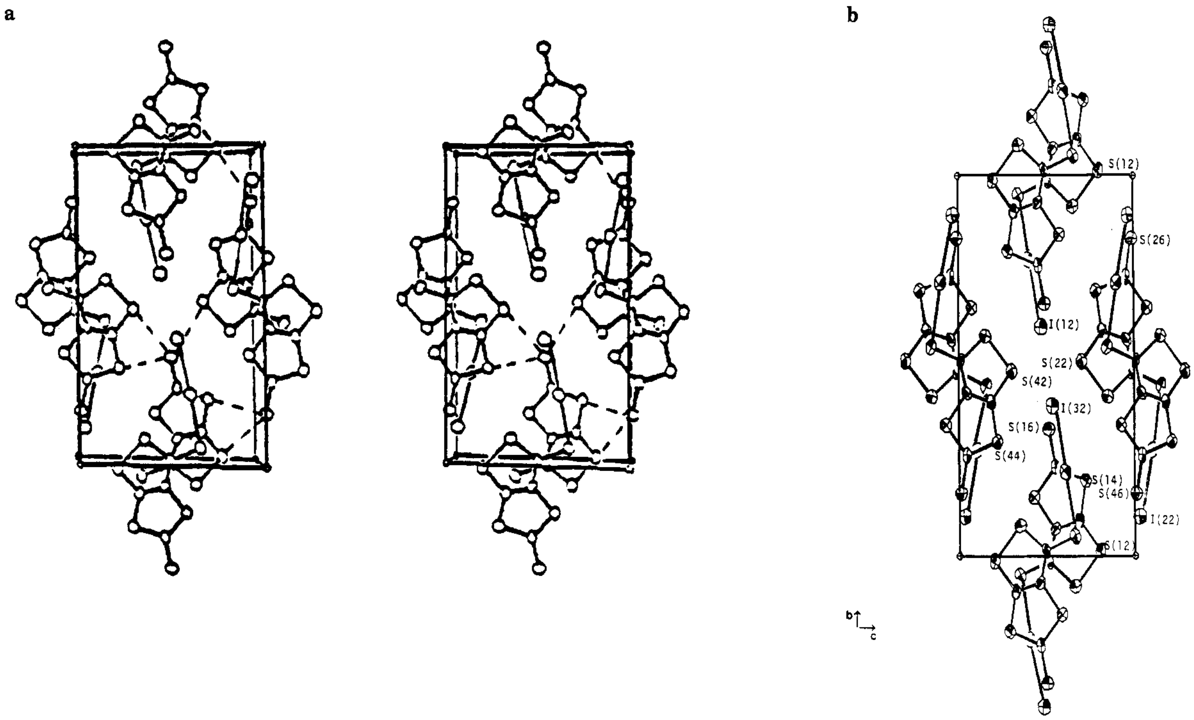


Figure 2. (a) Stereoview of a unit cell of $5 \cdot I_2$ showing the close intermolecular contacts with dashed lines. (b) View of one unit cell of $5 \cdot I_2$. The numbers in parentheses refer to Table III.

phases washed with dilute hydrochloric acid (1×) and water (2×). The solution was dried with magnesium sulfate and the ether, and most of the tetrahydrofuran was distilled carefully at atmospheric pressure (for a volatile ester) or removed by rotary evaporation (nonvolatile ester). All samples subjected to ^{1}H NMR, ^{13}C NMR, high resolution mass spectroscopy (HRMS), and elemental analysis were doubly thick-layer chromatographed and showed no spurious resonances in nuclear magnetic resonance spectroscopy. All NMR experiments are reported in ppm as δ relative to internal TMS and were recorded in $CDCl_3$, unless stated otherwise. IR spectra (KBr pellet for solids and neat film on NaCl disks for liquids) were recorded with a Perkin-Elmer Model 1330 spectrophotometer and are reported in wavenumbers (ν, cm^{-1}). UV-vis spectra were obtained with a Perkin-Elmer Model Lambda 5 instrument and are reported as λ nm (log ϵ).

Methyl Dithioacetate. Addition of carbon disulfide (9.0 mL, 154 mmol) to a solution of methylmagnesium bromide (40 mL of 3.0 M in ether) in tetrahydrofuran (150 mL) produced a clear red-orange solution attended by a modest exotherm. After the reaction was stirred for 3 h, addition of methyl iodide (9.0 mL, 145 mmol) discharged the orange color and slowly produced a white precipitate in a yellow solution. After the mixture was stirred for 4 h, the reaction was quenched by the slow addition of water (150 mL), and the organic phase was separated. The aqueous phase was extracted with pentane (2 × 100 mL); the combined organic phases were washed copiously with water (8 × 100 mL) to remove the tetrahydrofuran and dried with magnesium sulfate overnight. Distillation of the pentane through a short Vigreaux left an orange residue, which was distilled at reduced pressure (45–58 °C, 30 ± 5 Torr) to give methyl dithioacetate (10.4g, 98.1 mmol, 82%). HRMS: 105.9923, calcd for $C_3H_6S_2$ 105.9912. ^{1}H NMR: δ 2.62 (s, 3 H), 2.86 (s, 3 H). ^{13}C NMR: δ 20.28, 38.59, 233.12. IR: 2910, 1415, 1360, 1195, 1100, 865 cm^{-1}.

Ethyl Dithioacetate. After the Grignard–carbon disulfide mixture was stirred for 5 h, it was treated with a 2% excess of freshly distilled ethyl iodide. Within 20 h a large amount of white precipitate had formed, and the reaction was quenched with water (200 mL), followed by standard workup. Distillation of the resulting orange oil at the aspirator (35 ± 5 Torr, 52–54 °C) gave ethyl dithioacetate (8.88 g, 74 mmol, 62%). HRMS: 120.0073, calcd for $C_4H_8S_2$ 120.0068. ^{1}H NMR: δ 1.32 (t, 7.7 Hz, 3 H), 2.82 (s, 3 H), 3.20 (q, 7.7 Hz, 2 H). ^{13}C NMR: δ 12.11, 31.26, 39.14, 233.11. IR: 2970, 2925, 2870, 1195, 1100, 865 cm^{-1}.

Benzyl Dithioacetate. After the Grignard–carbon disulfide reaction mixture was stirred for 3 h, it was treated with a 1% excess of freshly distilled benzyl bromide, and the reaction mixture was left to stir overnight. Addition of water (40 mL) dissolved the precipitated salts, and the organic layer was separated and dried with sodium sulfate. Rotary evaporation of the tetrahydrofuran left an orange residue, which was distilled to give benzyl dithioacetate (bp 69–72 °C, Torr, 21.1 g, 116 mmol, 97%) in a single fraction. HRMS: 182.0216, calcd for $C_9H_{10}S_2$ 182.0225. ^{1}H NMR δ 2.82 (s, 3 H), 4.42 (s, 2 H), 7.27 (s, 5 H). ^{13}C NMR: δ 38.67, 41.81, 127.46, 128.5, 128.9, 134.96, 231.84. IR: 3080, 3045, 1505, 1460, 1210, 1190, 870 cm^{-1}.

5-(Methylthio)-1,2-dithiole-3-thione (1). To a suspension of sodium hydride (60% in oil, washed with hexane 2 × 15 mL; 1.0 g, 25 mmol) in tetrahydrofuran (20 mL) was added carbon disulfide (1.0 mL, 17 mmol) and then methyl dithioacetate (1.33 g, 10.0 mmol) in tetrahydrofuran (20 mL). The resulting mixture evolved hydrogen gas, turned from yellow to orange to burnt-orange, and was left to stir overnight. Addition of iodine (2.54 g, 10.0 mmol) dissolved in tetrahydrofuran (20 mL) discharged the orange color and produced a blue-black solution. After 4 h of stirring at room temperature, addition of water destroyed the small excess of sodium hydride and from the solution precipitated 5-(methylthio)-3-thioxo-1,2-dithiole 0.61 g, 3.4 mmol, 34%). Mp: 167–169 °C. HRMS: 179.9190, calcd for $C_4H_4S_4$ 179.9197. ^{1}H NMR: δ 2.69 (s, 3 H), 6.99 (s, 1 H). ^{13}C NMR: δ 17.31, 133.91, 178.43, 211.80. IR: 3055, 2970, 1465, 1320, 1185, 920 cm^{-1}.

5-(Ethylthio)-1,2-dithiole-3-thione. To a suspension of sodium hydride (60% in oil, washed with hexane 2 × 15 mL; 0.75 g, 18 mmol) in tetrahydrofuran (20 mL) was added carbon disulfide (0.5 mL, 8.5 mmol), and then ethyl dithioacetate (1.02 g, 8.5 mmol) in tetrahydrofuran (20 mL) was added in four portions over 15 min. Stirring for 6 h left a burnt-orange suspension, which was treated with a solution of iodine (2.16 g, 8.5 mmol) in tetrahydrofuran (20 mL) and left to stir overnight. After 18 h of stirring, the solvent was removed by rotary evaporation, and the residue was partitioned between ether (200 mL) and water (200 mL). The ether solution was dried with sodium sulfate and evaporated to a semisolid, which was extracted with boiling ethanol and left to cool, giving 5-(ethylthio)-3-thioxo-1,2-dithiole (mp 68–68.5 °C, 0.48 g, 2.5 mmol, 13%). HRMS: 193.9347, calcd for $C_5H_6S_4$ 193.9354. ^{1}H NMR: δ 1.47 (t, 7.4 Hz, 3 H), 3.15 (q, 7.4 Hz, 2 H), 7.00 (s, 1 H). ^{13}C NMR: δ 13.98, 30.04, 135.09, 174.37, 212.63. IR: 3050, 2970, 2920, 1455, 1315, 1180, 1040, 910 cm^{-1}.

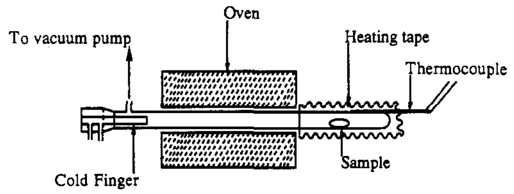


Figure 3. FVP Apparatus.

Anal. Calcd for $C_5H_6S_4$: C, 30.90; H, 3.12; S, 65.98. Found: C, 31.46; H, 2.65; S, 66.21.

5-(Benzylthio)-1,2-dithiole-3-thione. To a suspension of sodium hydride (60% in oil, washed with hexane 2 × 15 mL) (1.0 g, 25 mmol) in tetrahydrofuran (20 mL) was added carbon disulfide (1.0 mL, 17 mmol), and then benzyl dithioacetate (1.82 g, 10.0 mmol) in tetrahydrofuran (20 mL) was added. The slightly exothermic reaction mixture turned from yellow to orange to burnt-red over 2 h at which time iodine (2.6 g, 10 mmol) in tetrahydrofuran (10 mL) was added in four portions over 30 min. After the mixture was stirred overnight, rotary evaporation removed the volatiles, and the residue was taken up in a minimum of benzene. Addition of hexane precipitated the product, which was subsequently recrystallized from ethanol to give 5-(benzylthio)-1,2-dithiol-3-thione (mp 117–118 °C, 0.31 g, 1.21 mmol, 12%). HRMS: 255.9508, calcd for $C_{10}H_8S_4$ 255.9510. ^{1}H NMR: δ 4.32 (s, 2 H), 7.01 (s, 1 H), 7.38 (m, 5 H). ^{13}C NMR: δ 40.15, 128.54, 128.91, 129.05, 133.91, 136.09, 172.87, 212.77. IR: 3025, 1445, 1300, 1185, 1040, 910, 705, 655 cm^{-1}. Anal. Calcd for $C_{10}H_8S_4$: C, 46.84; H, 3.15; S, 50.01. Found: C, 47.34; H, 2.78; S, 50.12.

Dithiolodithiole (5). Heterocycle **4** (59 mg, 0.22 mmol) was loaded into a horizontally disposed FVP apparatus depicted in Figure 3. The apparatus was evacuated to $\leq 10^{-4}$ Torr and the oven was heated to ~600 °C while the sample compartment was heated to ~145 °C. The pyrolysis was allowed to proceed for 24 h. The product was extracted from the cold finger with refluxing toluene to afford 18 mg of a crude, multicomponent (TLC) product. This material was chromatographed on silica gel with toluene as eluent. The main fraction (6 mg) was a single spot with some trailing by TLC. Recrystallization from toluene afforded 3.9 mg of pure material as red crystals, mp 205–206 °C. HRMS calcd for C_4S_6 239.8324, found 239.8313446 (P^+). LRMS: 239.8 (P^+, 68.5), 163.8 ($P^+ - CS_2$, 20.0), 99.9 [$P^+ - CS_4 = C_3S_2$ (carbon subsulfide), 100], 87.9 (C_2S_2, 29.2), 75.9 (CS_2, 41.2), 64.0 (S_2, 11.0), 44 (CS, 7.8). IR (KBr) 1435, 1295, 1060, 880 w, 490 w cm^{-1}. UV–vis (CH_2Cl_2) 370.5 (4.09), 430 (3.96), 447 (3.95). The compound undergoes photobleaching upon irradiation with broad band UV light.

Methyl 5-(Methylthio)-2-thioxo-1,3-dithiole-4-dithiocarboxylate (3). Method A. To a suspension of dithiolo dithiole **5** (50.0 mg, 0.200 mmol) in dry THF (3 mL) was added dropwise 0.40 mL of a 1 M solution in THF of lithium triethylborohydride at 0 °C. After 10 min at 0 °C, followed by 10 min at room temperature, methyl iodide (0.37 mL 4.00 mmol) was added via syringe, and the reaction mixture was stirred at room temperature for 4 h. The solvent was removed by rotary evaporation, and the brown residue was washed with water and extracted with dichloromethane, and the organic layer was dried over anhydrous magnesium sulfate. Evaporation under reduced pressure afforded **3** in quantitative yield. Recrystallization from ethanol afforded organe crystals whose IR spectrum was identical with **3** prepared according to Scheme II.

Method B (Scheme II). To a suspension of 0.68 g, 16.9 mmol of sodium hydride (60% in oil, washed with hexane 2 × 20 mL) in tetrahydrofuran (20 mL) was added 0.69 mL (11.6 mmol) of carbon disulfide and then dimethyl tetrathiomalonate (1.51 g, 7.7 mmol) in 10 mL of tetrahydrofuran. The resulting mixture evolved hydrogen gas and turned from yellow to dark red over a period of 45 min. Addition of iodine (2.01 g, 7.9 mmol) dissolved in tetrahydrofuran (15 mL) discharged the dark red color and produced an orange-red solution. After 4 h of stirring at room temperature, addition of a solution of 11.0 g of sodium bisulfite in 500.0 mL of water caused the precipitation of compound **3**. The precipitate was washed with water and dried under high vacuum to produce 0.93 g, 45% yield of crude product. Flash chromatography on 200 g of silica gel with carbon tetrachloride as eluent gave a fast-moving fraction (28%), which was recrystallized from cyclohexane; mp 148–150 °C. HRMS: 271.9 (3.5), 269.9 (13.3), 256.9 (27), 254.9 (100), 210.9 (13.0), 146.9 (14.0), 115.0 (23.5), 99.9 (40.8), 91.0 (24.0), 75.9 (14.5), 71.0 (5.6), 45.0 (12.6). ^{1}H NMR (carbon disulfide): δ 2.63 (s), 2.69 (s). IR: 1425 s, 1325 w, 1305 w, 1235 m, 1215 m, 1070 s, 1010 s, 935 w, 895 m, 830 w, 715 w. Anal. Calcd for $C_6H_6S_6$: C, 26.64; H, 2.24; S, 71.12. Found: C, 26.82; H, 2.22; S, 71.00.

Crystal Structure Determination. When a hot solution of **5** in acetonitrile was treated with an excess of iodine and allowed to cool slowly, purple needles with a metallic luster were obtained. Unfortunately most of these were twinned, but nonetheless a small crystal suitable for X-ray diffraction was found within this batch. The crystal was mounted on the Huber four-circle automatic diffractometer with a graphite monochromator. The unit cell dimensions were obtained from the least-squares refinement for 35 reflections ($\theta < 13°$). The crystal data are summarized in Table I.

Intensities were collected by the $\theta - 2\theta$ scan technique using Mo Kα radiation ($\lambda = 0.71069$ Å); three standard reflections were monitored after every 97 reflections, and no significant fluctuations in their intensities were observed. The total of 925 unique reflections with $I > 3\sigma(I)$ were collected. The data were corrected for Lorentz polarization but not for absorption effects. The two iodine atoms were found by combining Patterson and Direct methods (UCLA Crystallographic computing package, C. E. Strousse). All remaining atoms from the asymmetric unit were found from the first difference Fourier map, with isotropic refinement giving $R = 0.124$ and $R_w = 0.14$. The full-matrix least-squares anisotropic refinement converged to $R = 0.054$ and $R_w = 0.062$ ($R_w = [(\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2}]$).

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