

Preparation and Properties of Novel Sulphur Heterocycles from the Reaction of 4,5-Disubstituted 2-Lithio-1,3-dithioles with Carbon Disulphide and X-Ray Crystallographic Structure of 2-(4,5-Dimethyl-1,3-dithiolyldiene)-5,6-dimethyl-2,3-dihydro-1,4-dithiine-3-thione

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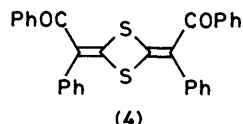
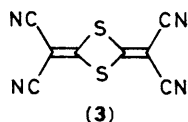
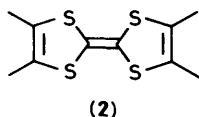
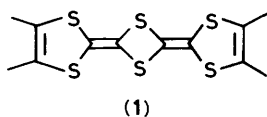
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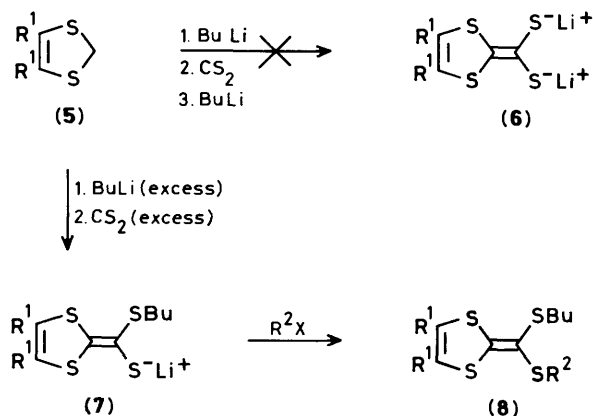
The reaction of 4,5-disubstituted 2-lithio-1,3-dithioles with carbon disulphide followed by treatment with ethyl chloroformate or methyl iodide produces a new type of heterocyclic system. Spectral and analytical data indicated that the molecule consists of a five-membered 1,3-dithiole ring conjugated to an expanded six-membered ring, derived from the former by the insertion of a thiocarbonyl group (9). Single-crystal X-ray diffraction unequivocally identified the 4,5-dimethyl compound (9a): triclinic, $P\bar{1}$, with $a = 7.852(6)$, $b = 12.253(22)$, $c = 7.807(12)$ Å, $\alpha = 78.02(13)$, $\beta = 110.29(10)$, $\gamma = 91.11(11)^\circ$ and $Z = 2$. The five-membered ring is planar but the six-membered ring is folded. Short intramolecular C=S...S contacts (3.082 Å) indicate partial bonding between those two sulphur atoms, resulting in a 'no-bond' aromatic system isoelectronic with naphthalene.

The intensive search for new electron donors¹⁻⁴ has produced many new and unusual systems, some of which have most interesting properties. While variants and derivatives of tetrathia-(TTF), tetraselena-(TSF), and tetratellura-fulvalene (TTeF) still play a major role in this field, other promising candidates have been synthesized. A long standing target⁵ is the desaurine-like compound (1) which is formally obtained by insertion of the 1,3-dithietane unit into the tetramethyl tetrathiafulvalene molecule (2). An electron-acceptor of this type, (3), which is isoelectronic with tetracyanoquinodimethane was synthesized some time ago⁶ and it was felt that compounds of type (1) might exhibit interesting electron-donor properties and even form conducting ion-radical solid salts. Simple desaurines [e.g. (4)] are usually synthesized by condensing an active methylene compound with carbon disulphide in the presence of base, and then allowing the dithioate dianion so formed to react with acylating⁷⁻⁸ or oxidizing⁹ agents.



In order to follow this procedure for the synthesis of compound (1), the dithioate (6) must be prepared. However, we have recently shown¹⁰ that the reaction of a 4,5-disubstituted 1,3-dithiole (5) with butyl-lithium followed by addition of CS₂, and a second equivalent of the strong base does not lead to the dithioate (6). A competing thiophilic addition leading to the intermediate anion (7) takes place and, after alkylation, the bis-alkylthio-1,3-dithioles (8) are isolated.

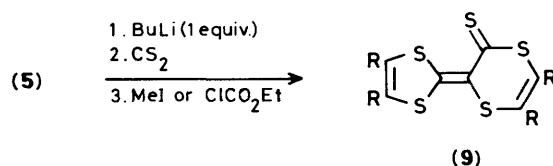
Thus, a more controlled route for the formation of the synthon (6) was needed. We first attempted to quench the



reaction and examine possible early intermediates. During those attempts we were able to isolate in high yield and characterize a new type of heterocyclic system which is the subject of this report.

Results and Discussion

Synthesis and Physical Properties.—Reaction of the 1,3-dithiole (5) with 1 equiv. of butyl-lithium at -30°C followed by carbon disulphide and then immediate quenching of the mixture with an excess of methyl iodide gave rise to a strong red colour which intensified upon warming to room



(9a; R = Me)

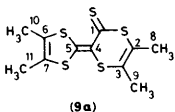
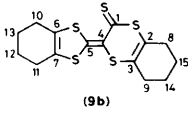
(9b; R = CH₂(CH₂)₂CH₂)

Table 1. Physical and spectroscopic data of compounds (9)

Entry	Recryst. solvent	M.p. (°C)	Yield (%)	$\nu_{\max.} \text{cm}^{-1} \text{ } ^a$	$10^3 \lambda_{\max.}/\text{nm}$ ($\epsilon \times 10^{-3}$)	$\delta_{\text{H}} \text{ } ^b$	$m/z \text{ } ^c$
(9a)	Toluene	219—220	79	{ 1 625(C=C), 1 610(C=C) 1 370(C=S), 950	{ 252(15) 309(6.1) 399(3.6) 495(17)	2.0 (3 H, s, Me), 2.13 (3 H, s, Me)	304 (M^+ , 100%)
					{ 254(12) 308(6.8) 404(4.5) 498(17)	2.18 (3 H, s, Me), 2.24 (3 H, s, Me)	131 (26)
(9b)	Ethyl acetate	222—223	61	{ 1 630(C=C), 1 610(C=C) 1 375(C=S), 950	{ 254(12) 308(6.8) 404(4.5) 498(17)	1.66—1.98 [8 H, m, 4(CH ₂)]	356 (M^+ , 100%)
					{ 254(12) 308(6.8) 404(4.5) 498(17)	2.25—2.7 [8 H, m, 4(CH ₂)]	157 (19)

^a KBr pellet. ^b Chemical shift value (δ) observed in p.p.m. relative to Me₄Si, followed by the multiplicity of the signal. ^c Recorded on a NERMAG R10—10 spectrometer; % relative abundance assignment are given.

Table 2. δ_{C} Chemical shifts of (9) in CDCl₃^a

Compd.	$\delta^{13}\text{C}$ for indicated carbons							
	1	2	3	4	5	6,7	8,9	10,11
 (9a)	199.48	132.16	129.36	165.87	114.91	{ 125.31 128.15	{ 18.34 19.85	{ 14.85 15.12
 (9b)	199.49	134.16	132.02	166.02	115.05	{ 127.56 130.59	{ 30.24 31.99	{ 29.94 ^b 25.72

^a The chemical shifts are in p.p.m. relative to Me₄Si. ^b $\delta^{13}\text{C}$ For carbons 12, 13, 14, and 15 are: 22.36, 22.47, 22.81, 23.03.

Table 3. Cyclic voltammetry data of (9)^a

Compd.	1st Redox couple			2nd Redox couple			3rd Redox couple		
	$E_{\text{p1}}^{\text{red}}$	$E_{\text{p1}}^{\text{ox}}$	$E_{1/2}^1$	$E_{\text{p2}}^{\text{red}}$	$E_{\text{p2}}^{\text{ox}}$	$E_{1/2}^2$	$E_{\text{p3}}^{\text{red}}$	$E_{\text{p3}}^{\text{ox}}$	$E_{1/2}^3$
(9a)	0.56	0.95	0.76	1.56	1.66	1.61	-1.27	-1.17	-1.22
(9b)	0.58	0.96	0.77	1.55	1.65	1.60	-1.24	-1.16	-1.20
TMTTF	0.34	0.42	0.38	0.82	0.92	0.87			

^a In CH₂Cl₂ 0.1M Bu₄NPF₆, on platinum working and counter electrodes. All potentials are quoted vs. SCE reference electrode. Sweep rate = 100 mV/s; E_1 is defined as $1/2 (E_{\text{p}}^{\text{red}} + E_{\text{p}}^{\text{ox}})$. All quoted potentials are average 2—3 separate runs.

temperature. Work-up of the mixture afforded a red solid in high yield to which we assigned structure (9). An identical reaction, with higher reaction rate, took place when methyl iodide was replaced by ethyl chloroformate. A very low yield of a presumably similar aromatic product was isolated from a complex reaction mixture derived from 1,3-benzodithiole.⁵

The spectral and analytical data, summarized in Tables 1 and 2 strongly support structure (9) as best representing these compounds. ¹H N.m.r. results suggest an unsymmetrical system with different environment (δ 2.0—2.3) for the four methyl protons in (9a) or the methylene protons in (9b).

The parent peak in the mass spectrum is also the base peak and the fragmentation pattern shows the 4,5-disubstituted dithiolium ions [131 for (9a) and 157 for (9b)] as the most intense peaks. The inserted C=S group can be seen in the i.r. region as very strong absorption at 1 370 cm⁻¹. ¹³C N.m.r. spectral results are also in agreement with structure (9) (see Table 2). Here the assignments were made by comparison with the tetrathiafulvalene molecule,¹¹ other closely related systems, and pertinent literature.¹² The carbon numbering scheme is as shown in Table 2. The characteristic singlet of the C=S group

appears around δ 199. The four endocyclic sp² carbons occur as expected, as singlets in the range δ 125—135, while the two exocyclic sp² carbons differ considerably; although C-5 appears at δ 115, a position similar to that for the equivalent carbon in TTF (δ 110), C-4 shows an exceptional downfield shift (δ 166) as a result of being strongly deshielded by the C=S group.

Table 3 shows cyclic voltammetric data for compounds (9), and for reference we have listed the analogous potentials for (TMTTF) as well. The data show two redox potentials at significantly higher potentials as compared with the corresponding waves for TMTTF. In addition, a third quasi-reversible reduction wave of negative potentials ($E_1^3 \sim -1.2$ V) is observed and is probably related to the reduction of the C=S group in the six-membered ring.

Molecular Structure.—The structure of (9a) differs significantly in its conformation from that of TMTTF.¹³ Thus, in virtually all structures the TMTTF has a planar structure with all the four methyl carbon atoms lying in the plane of the TTF moiety. In the present case, the molecule consists of a five-membered ring similar to that of TMTTF and a six-membered

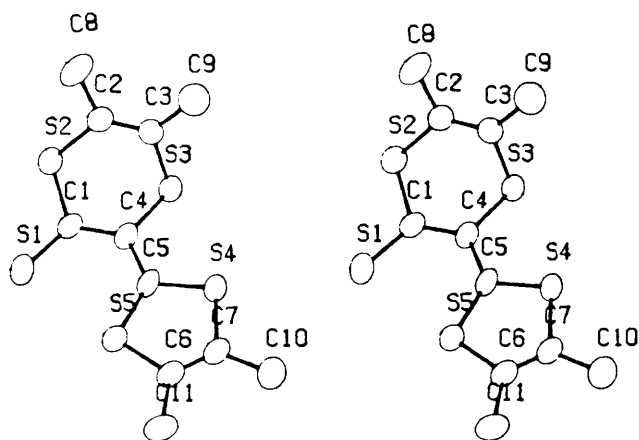


Figure 1. ORTEP stereo diagram of molecule (9a) showing the atomic numbering of the non-hydrogen atoms

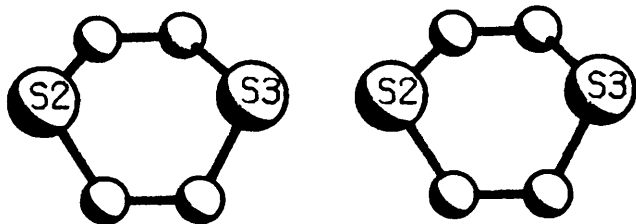


Figure 2. Stereoview of the six-membered ring, showing the folding about the S(2)-S(3) axis

ring derived from the former by the insertion of a thiocarbonyl group. The five-membered ring is planar and the two methyl groups connected to this ring also lie in the plane of the ring. The deviations of C(10) and C(11) atoms (Figure 1) from the five-membered ring are 0.028(7) and 0.025(7) Å respectively.

The six-membered ring is not planar as the result of folding about an axis through atoms S(2) and S(3). This leads to an angle of 49.7° between the plane defined by atoms S(2), C(2), C(3), and S(3) and that defined by S(2), C(1), C(4), and S(3). The bond angles at S(2) and S(3) are 106.1 (2) and 102.1 (2)° respectively. Figure 2 illustrates the folding of the six-membered ring of the molecule.

The C-S bond lengths in both rings also differ considerably. The average C-S distance in the five-membered ring is 1.746(5) Å; the bond length, S(4)-C(6) and S(5)-C(7) are 1.752(5) and 1.764(5) Å respectively, longer than those observed for C(5)-S(4) and C(5)-S(5), 1.733(5) and 1.734(5) Å respectively. The C-S distances in the six-membered ring average 1.782(5) Å with a small scatter, a value which is longer than those found in the other ring (Table 6). The non-bonded intramolecular S(1)⋯S(5) distance is 3.082 Å and the dihedral angle between the five-membered ring and the plane defined by S(1), S(2), S(3), C(1), and C(4) is only 10°. This distance is considerably shorter than twice the van der Waals radius of sulphur indicating partial bonding between the two sulphur atoms. Moreover, the difference between the C-S distances in the two rings, the length of the C(1)-C(4) bond, and the molecular folding suggest that the five-membered ring is in conjugation with the thiocarbonyl group and the six-membered as a whole is not involved in any conjugation. This may be interpreted by suggesting that the resonance structure represented by (I) is a significant contributor to the electronic structure.

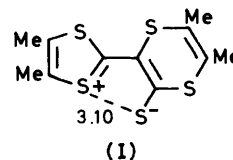
Such a structure resembles the 'no-bond resonance' systems

Table 4. Fractional co-ordinates $\times 10^4$ of molecule (9a), e.s.d. in terms of the least significant digit is given in parentheses

Atom	x	y	z
S(1)	1 930(2)	1 505(1)	-4 677(2)
S(2)	3 196(2)	3 633(1)	-3 615(2)
S(3)	4 675(2)	2 493(1)	0 648(2)
S(4)	3 475(2)	0 234(1)	2 151(2)
S(5)	1 816(2)	-0 342(1)	-1 477(2)
C(1)	2 836(6)	2 186(4)	-2 954(6)
C(2)	2 820(6)	4 288(4)	-1 926(7)
C(3)	3 404(6)	3 795(4)	-0 119(7)
C(4)	3 362(6)	1 721(4)	-1 006(6)
C(5)	2 915(6)	0 649(4)	-0 249(6)
C(6)	2 534(6)	-1 074(4)	2 150(7)
C(7)	1 741(6)	-1 334(4)	0 484(7)
C(8)	1 772(11)	5 412(6)	-2 783(12)
C(9)	3 076(12)	4 262(7)	1 391(11)
C(10)	2 722(10)	-1 777(6)	4 062(10)
C(11)	0 820(10)	-2 402(5)	0 089(11)
H8(A)	1 701(115)	5 698(74)	-3 949(133)
H8(B)	1 994(116)	5 848(70)	-1 894(128)
H8(C)	0 483(114)	5 301(60)	-3 051(106)
H9(A)	3 981(142)	4 204(80)	2 463(149)
H9(B)	2 394(111)	3 909(64)	1 784(113)
H9(C)	2 516(116)	5 017(74)	0 846(125)
H1(0A)	3 838(138)	-1 745(75)	5 024(147)
H1(0B)	2 337(170)	-2 501(114)	3 935(175)
H1(0C)	2 009(126)	-1 519(75)	4 685(134)
H1(1A)	-0 252(161)	-2 332(93)	-0 673(162)
H1(1B)	0 167(134)	-2 618(77)	1 202(137)
H1(1C)	1 572(91)	-2 883(56)	0 422(95)

Table 5. Bond lengths in molecule (9a), e.s.d. in terms of the last significant digit is given in parentheses

S(1)-C(1)	1.671(5)	S(2)-C(1)	1.787(5)
S(2)-C(2)	1.786(5)	S(3)-C(3)	1.775(5)
S(3)-C(4)	1.781(5)	S(4)-C(5)	1.733(5)
S(4)-C(6)	1.752(5)	S(5)-C(5)	1.734(5)
S(5)-C(7)	1.764(5)	C(1)-C(4)	1.422(6)
C(2)-C(3)	1.332(7)	C(2)-C(8)	1.517(9)
C(3)-C(9)	1.510(9)	C(4)-C(5)	1.415(7)
C(6)-C(7)	1.335(7)	C(6)-C(10)	1.520(9)
C(7)-C(11)	1.519(8)	C(8)-H(8A)	0.89(9)
C(8)-H(8B)	0.93(9)	C(8)-H(8C)	0.97(8)
C(9)-H(9A)	0.88(10)	C(9)-H(9B)	0.79(8)
C(9)-H(9C)	0.98(8)	C(10)-H(10A)	0.94(9)
C(10)-H(10B)	0.95(13)	C(10)-C(10C)	0.95(9)
C(11)-H(11A)	0.84(12)	C(11)-H(11B)	1.14(9)
C(11)-H(11C)	0.78(8)		



which were first discovered in thiothiophenes.¹⁴ This might contribute to stabilization of the conformation (I) through formation of two condensed five-membered rings, isoelectronic with naphthalene.

Even though the molecule contains five sulphur atoms which generally have a tendency to be involved in many intermolecular interactions, few short S⋯S intermolecular distances are observed. The only notable S⋯S close contact below or in the range of the sum of their van der Waals radii are

Table 6. Bond angles in molecule (9a), e.s.d. in terms of the last significant digit is given in parentheses

S(2)-C(1)-S(1)	117.1(3)	C(4)-C(1)-S(1)	126.2(4)
C(4)-C(1)-S(2)	116.8(3)	C(1)-S(2)-C(2)	106.1(2)
S(2)-C(2)-C(3)	121.3(4)	S(2)-C(2)-C(8)	113.0(4)
C(8)-C(2)-C(3)	125.7(5)	C(2)-C(3)-S(3)	119.6(4)
C(2)-C(3)-C(9)	124.9(5)	C(9)-C(3)-S(3)	115.6(4)
C(3)-S(3)-C(4)	102.1(2)	C(1)-C(4)-S(3)	120.1(4)
S(3)-C(4)-C(5)	115.9(3)	C(1)-C(4)-C(5)	124.0(4)
C(4)-C(5)-S(4)	119.1(3)	C(4)-C(5)-S(5)	126.9(3)
S(4)-C(5)-S(5)	114.0(3)	C(5)-S(4)-C(6)	96.7(2)
S(4)-C(6)-C(7)	116.6(4)	S(4)-C(6)-C(10)	115.6(4)
C(10)-C(6)-C(7)	127.9(5)	C(6)-C(7)-S(5)	116.5(4)
C(6)-C(7)-C(11)	127.3(5)	C(11)-C(7)-S(5)	116.2(4)
C(7)-S(5)-C(5)	96.2(2)	C(2)-C(8)-H(8A)	114(6)
C(2)-C(8)-H(8B)	110(5)	C(2)-C(8)-H(8C)	109(4)
C(3)-C(9)-H(9A)	118(8)	C(3)-C(9)-H(9B)	111(5)
C(3)-C(9)-H(9C)	109(5)	C(6)-C(10)-H(10A)	116(6)
C(6)-C(10)-H(10B)	109(7)	C(6)-C(10)-H(10C)	116(6)
C(7)-C(11)-H(11A)	117(8)	C(7)-C(11)-H(11B)	103(5)
C(7)-C(11)-H(11C)	108(5)		

3.646(2) Å for S(3) (x, y, z) and S(5) ($1-x, -y, -z$) and 3.713(3) Å for S(1) (x, y, z) and S(4) ($x, y, -1+z$); no other short contacts are present.

In conclusion, while additional studies are needed to obtain the desaurine-like compounds (1), we have synthesized and determined the structure of a new type of interesting heterocyclic system. The mechanism by which these compounds are formed and the scope of this unusual reaction are currently being studied.

Experimental

General Methods.—M.p.s were determined on a Kofler Heizbank apparatus and are uncorrected. I.r. spectra were recorded on Beckman IR spectrophotometer. N.m.r. spectra were taken on a Perkin-Elmer R 32 or a Bruker AM 250 MHz instrument as solutions in CDCl_3 using tetramethylsilane as internal standard. U.v. spectra were taken in MeOH on a Varian Cary 219 apparatus. Cyclic voltammetry was carried out on a EG & G PAR 273 Potentiostat and a Sefram TGM 164 X-Y recorder. Elemental analyses were determined by the Microanalytical Laboratory of the CNRS at Gif sur Yvette. Purum THF was dried over ICN Alumina B-Super I immediately prior to use. The 4,5-disubstituted 1,3-dithioles (5) were prepared by reduction of the appropriate 1,3-dithiole-2-thiones according to the literature method.¹⁵ All reactions were executed under an atmosphere of dry argon using oven-dried glassware.

Crystal Data.— $\text{C}_{11}\text{H}_{12}\text{S}_5$, $M = 304$, Triclinic, space group $P\bar{1}$, $a = 7.852(6)$, $b = 12.253(22)$, $c = 7.807(12)$ Å, $\alpha = 78.02(13)$, $\beta = 110.29(10)$, $\gamma = 91.11(11)^\circ$, $V = 688.1(19)$ Å³, $F(000) = 316$, $\mu(\text{Mo-K}\alpha) = 7.39 \text{ cm}^{-1}$, $Z = 2$, $D_c = 1.47 \text{ g cm}^{-3}$ (Mo-K α , $\lambda = 0.71069$ Å). Unit cell parameters were determined by a least-squares fit of 15 accurately centred high-order reflections within limits $15 < 2\theta < 26^\circ$. 1855 Reflections were considered to be non-zero at the 4σ significance level out of the 2218 unique reflections in the range of $3 < 2\theta < 50^\circ$. No absorption corrections were applied and there was no evidence for crystal decomposition during the data collection. The weights were taken as $3.556/[\sigma(F_o)^2 + (0.02 F_o)^2]$ where $\sigma(F_o)$ is the standard deviation based on the counting statistics. Scattering factors for all elements were taken from the International Tables for X-ray Crystallography.¹⁶

The structure was solved by the Patterson vector search method using SHELX 86¹⁷ which yielded the positions of all non-hydrogen atoms. However, a parallel attempt to solve the structure by direct methods did not yield a solution. Least-square refinement by using SHELX 76¹⁷ began at an R value of 0.21 and converged to 0.099 for positional parameters and isotropic thermal parameters for all non-hydrogen atoms. When the positional and anisotropic thermal parameters for all non-hydrogen atoms are varied by using block-matrix least-square refinement method the R value was further lowered to a value of 0.069. At this stage the difference Fourier map revealed the positions of some of the hydrogen atoms and the rest of them were affixed and varied isotropically along with all other non-hydrogen atoms. Five reflections with indices (010), (011), (012), (112), and (0-31) which suffered from extinction were omitted from the final cycles of refinement. The final R factor is 0.057 and R_w is 0.059. The atomic co-ordinates are given in Table 4.

Figure 1 is the ORTEP stereodiagram of the molecule with the atomic numbering scheme and Tables 5 and 6 show the bond lengths and bond angles. The thermal parameters and torsion angles are available on request from the Cambridge Crystallographic Data Centre.*

2-(4,5-Dimethyl-1,3-dithiolydene)-5,6-dimethyl-2,3-dihydro-1,4-dithiine-3-thione (9a).—Butyl-lithium (1.6M in hexane; 6.5 ml, 10 mmol) was added dropwise with stirring to a solution of 4,5-dimethyl-1,3-dithiole (1.32 g, 10 mmol) in THF (150 ml) at -30°C . The solution was stirred for 45 min at the same temperature after which CS_2 (7.6 g, 0.1 mol) was added at once to yield an orange solution. Immediately, ethyl chloroformate (1.09 g, 10 mmol) was added and the mixture slowly warmed to room temperature (from this point anhydrous conditions were no longer necessary). The deep-red solution was evaporated under reduced pressure and water (100 ml) added to the residue; the mixture was then extracted with diethyl ether (3×80 ml). The combined extracts were dried (MgSO_4), evaporated under reduced pressure, and the residue recrystallized from toluene to yield dark red crystals of (9a) (2.4 g, 79%) (Found: C, 43.6; H, 3.9; S, 52.3. $\text{C}_{11}\text{H}_{12}\text{S}_5$ requires C, 43.4; H, 4.00; S, 52.65%).

2-(4,5,6,7-Tetrahydro-1,3-benzodithiol-2-ylidene)-2,3,5,6,7,8-hexahydro-1,4-benzodithiine-3-thione (9b).—Using the procedure described above, 4,5-tetramethylene-1,3-dithiole (1.58 g, 10 mmol) was treated with butyl-lithium (1.6M in hexane; 6.5 ml, 10 mmol), then with CS_2 (7.6 g, 0.1 mol), and finally ethyl chloroformate (1.09 g, 10 mmol). The product (2.2 g, 61%) was purified by flash chromatography on silica gel using toluene-hexane (3:1) and recrystallized from ethyl acetate (Found: C, 50.3; H, 4.4; S, 45.2. $\text{C}_{15}\text{H}_{16}\text{S}_5$ requires C, 50.5; H, 4.5; S, 45.0%).

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* See 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans 1*, 1988, Issue 1.

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