Methyl 2-Methyldithiocarbazate in Heterocyclic Synthesis: Preparation of 2,5-Disubstituted 1,3,4-Thiadiazoles, Bis(1,3,4-Thiadiazolium) Salts and Macrocycles containing 1,3,4-Thiadiazole Subunits. X-Ray Crystal Structure of 2,2'-Bis[4,5-dihydro-5-(2-hydroxyethylimino)-4-methyl-1,3,4-thiadiazole]

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Reaction of the iminophosphorane **2**, derived from methyl 2-methyldithiocarbazate and triphenylphosphine, with carbon disulphide gives the mesoionic compound **3**, which reacts with α,ω-dihalogeno compounds to give bis-(1,3,4-thiadiazolines) **7–9**. However, reaction with ethylenediamine or 1,4-tetramethylenediamine leads to macrocycles **11** and **12**. Methyl 2-methyldithiocarbazate, by sequential treatment with dicarboxylic acid chlorides and perchloric acid, leads to the bis-(1,3,4-thiadiazolium) salts **19–21**, which undergo nucleophilic displacement of the methylthio group, upon reaction with β-substituted ethylamines, to give products **22–28**. The crystal structure of compound **22** has been determined by X-ray crystallography. The crystal could be described in a *P*1 cell, with parameters a = 11.286 2(17), b = 7.740 9(8), c = 4.267 6(2) Å, α = 93.441(5), β = 91.703(6) and γ = 108.780(12)°. The molecule presents an internal crystallographic inversion centre, and the terminal OH groups are disordered between two tetrahedral positions of the bonded carbon atom.

Macrocycles containing heterocyclic subunits have been shown to possess interesting chemical and biochemical properties. In view of the limited examples of 1,3,4-thiadiazole inclusion in a macrocyclic framework,[1] we herein describe the synthesis and characterization of macrocycles containing 2,5-diamino-1,3,4-thiadiazole subunits connected by ethylene and 1,4-tetramethylene bridges, as well as their open-chain counterparts.

On the other hand, heteroarene oligomers constitute a class of heterocyclic compounds of increasing interest owing to their biological properties.[2] Methods for the preparation of heterocyclic dimers involve palladium-mediated oxidative dimerization of heteroarenes,[3] and metal-catalysed cross-coupling of heteroaryl halides with Grignard reagents,[4] boronic acids[5] or stannylheteroarenes.[6] Herein we report an efficient new method for the synthesis of the previously unreported bis-(1,3,4- thiadiazole) derivatives, which is based on the sequential treatment of methyl 2-methyldithiocarbazate with dicarboxylic acid chlorides and perchloric acid.

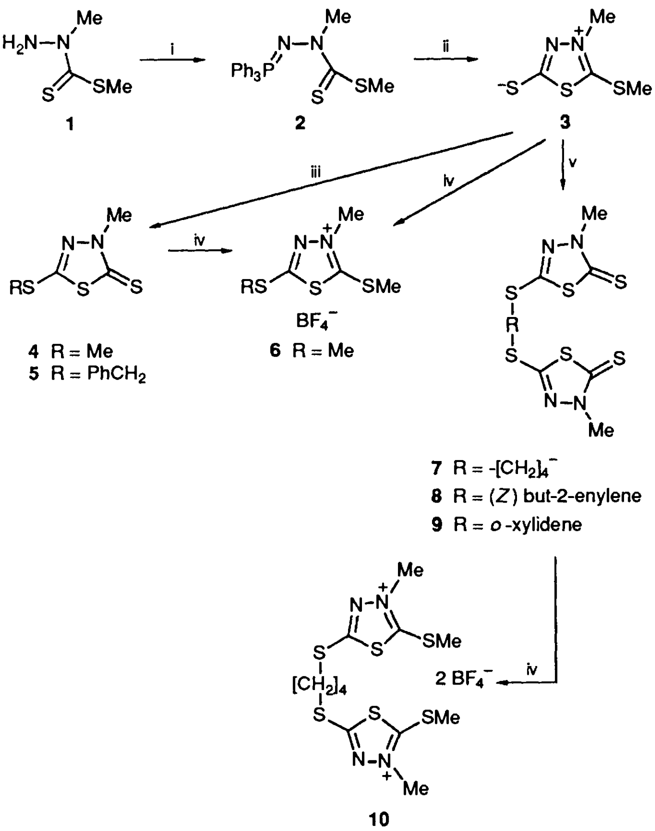
Results and Discussion

The iminophosphorane **2**, readily available from methyl 2-methyldithiocarbazate **1** and triphenylphosphine dibromide,[7] reacts with carbon disulphide at room temperature to give the mesoionic 4-methyl-5-methylthio-1,3,4-thiadiazolium-2-thiolate **3** as a crystalline solid in 81% yield. The IR spectrum of compound **3** shows a strong absorption band at 1362 cm^{-1} which can be attributed to exocyclic C–S stretching.[8] The absence of isothiocyanate bands provides support for the formulation of compound **3** as a cyclic mesoionic structure rather than as a valence tautomer. The ^1H NMR spectrum displays two singlets, at δ 2.82 and 3.79, due to the *S*-methyl and *N*-methyl groups, respectively. In the ^{13}C NMR spectrum, the quaternary carbons appear at δ_C 181.0 (C-2) and 167.8 (C-5), and the *S*-methyl and *N*-methyl group carbons appear at δ 19.6 and 40.6, respectively. The mass spectrum shows the expected molecular ion as the base peak and the fragmentation pattern is in accord with the proposed structure.

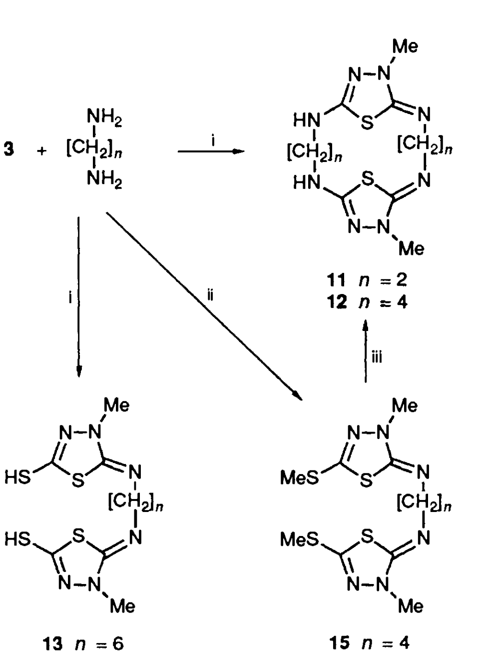
The conversion **2** ⟶ **3** presumably involves an initial aza-Wittig-type reaction between the iminophosphorane **2** and carbon disulphide to give an isothiocyanate as a highly reactive intermediate, which undergoes cyclization to afford the mesoionic compound **3**.

Compound **3** undergoes regioselective *S*-alkylation and subsequent demethylation by the action of methyl iodide or benzyl bromide to give the corresponding 5-alkylthio-3-methyl-1,3,4-thiadiazoline-2-thiones **4** and **5**. Compounds **3** and **4** undergo *S*-methylation upon reaction with Meerwein's reagent to yield the 3-methyl-2,5-bis(methylthio)-1,3,4-thiadiazolium salt **6**. Similarly, reaction of compound **3** with 0.5 mol equiv. of several α,ω-dihalogeno compounds in chloroform produces acyclic dimers **7–9** in good yield, which undergo *S*-methylation upon reaction with Meerwein's reagent to give unstable salts. Only compound **10** could be isolated and stored without any sign of decomposition (Scheme 1).

Compound **3** also reacts with α,ω-diaminoalkanes, and the nature of the reaction product appears to depend on the length of the diamine. When the high-dilution reaction of compound **3** and ethylenediamine or tetramethylenediamine is carried out in chloroform at reflux temperature for 6 h, in the presence of triethylamine, the corresponding [5,5']ylenediamino[2,2']-ylenediiminobis-(2,3-dihydro-3-methyl-1,3,4-thiadiazolino)-phanes **11** and **12** are obtained as crystalline solids in good yield. However, the use of hexamethylenediamine or octamethylenediamine, under the same reaction conditions, leads to dithiols **13** and **14** in good yield, according with the behaviour observed in the reaction of the related 3-methyl-2-methylthio-1,3,4-thiadiazolium cation with hydrazine, ethylenediamine and *o*-phenylenediamine.[9] Reaction of compound **3** with tetramethylenediamine in methylene dichloride at reflux temperature for 3 h, in the presence of methyl iodide, gives the 5,5'-bis(methylthio) derivative **15**, which by treatment with an ethanolic solution of tetramethylenediamine is converted into the macrocyclic compound **12** (Scheme 2), which clearly confirms the proposed structure **12** for the product of the reaction of compound **3** and tetramethylenediamine. Structure



Scheme 1 *Reagents and conditions:* i, $Ph_3P{\cdot}Br_2$; ii, CS_2, room temp., iii, RX; iv, Me_3O^+ BF_4^-; v, BrRBr



Scheme 2 *Reagents and conditions:* i, Et_3N, $CHCl_3$, reflux, 6 h; ii, Et_3N, MeI, CH_2Cl_2, reflux, 2 h; iii, $H_2N[CH_2]_4NH_2$, EtOH, reflux

12 was easily assigned by NMR spectroscopy. The ^1H NMR spectrum in $[^2H_6]$dimethyl sulphoxide displays two different triplets, at δ 2.82 for the CH_2NH and at δ 2.90 for the CH_2N=, while the central methylenes appear as a multiplet centred at δ 1.60 and the *N*-methyl appears as a singlet at δ 3.20. The ^{13}C NMR spectrum shows the two expected peaks for quaternary carbons at δ_C 159.2 (C-5) and 162.0 (C-2), four peaks for the methylenes at δ_C 25.7 and 27.9 (central CH_2), δ_C 39.0 (CH_2NH) and δ_C 55.3 (CH_2N=), in addition to the *N*-methyl group carbon at δ_C 34.4. The proton and carbon chemical-shift values in structure **12** are consistent with those previously observed for the open-chain analogues.[7-9]

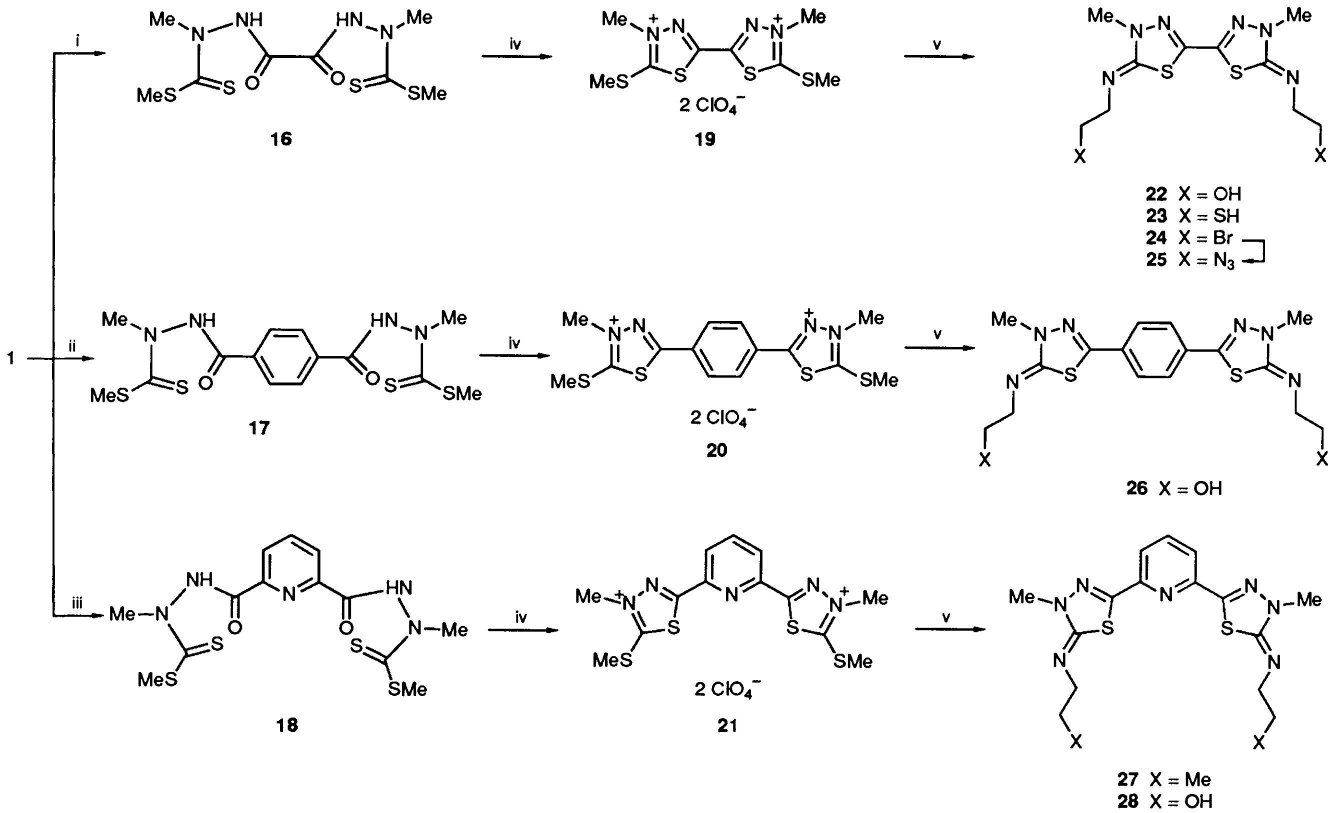
In the ^1H NMR spectrum of compound **15**, the *N*-methyl and *S*-methyl signals appear as singlets at δ 3.86 and 2.67, respectively, while the methylene groups appear at δ 1.79 (central CH_2) and 3.34 (CH_2N=). In the ^{13}C NMR spectrum the quaternary carbons appear at δ_C 152.0 (C-5) and 166.1 (C-2), and the methylene carbons occur at δ_C 24.8 (central CH_2) and 50.7 (CH_2N=). The mass spectrum gave a parent peak at *m/z* 376, and the fragmentation pattern is in agreement with the proposed structure.

On the other hand, compound **1** undergoes acylation upon reaction with diacyl chlorides to give acyclic derivatives. Thus, reaction of compound **1** with oxalyl dichloride, terephthaloyl dichloride, and pyridine-2,6-dicarboxylic dichloride leads to compounds **16**–**18**, respectively, in excellent yield (86–98%). These compounds undergo cyclization with perchloric acid–acetic anhydride in dry diethyl ether at room temperature to give the salts **19**–**21** in excellent yield (87–91%). The ^1H NMR spectra of compounds **19**–**21** show two sharp singlets, at δ 3.15–3.20 and 4.23–4.26, due to the *S*- and *N*-methyl groups, respectively. In the ^{13}C NMR spectra, the quaternary carbons appear at δ_C 163.4–165.6 (C-2) and at 180.3–182.7 (C-5), while the *S*- and *N*-methyl groups carbons occur at δ_C 20.6–21.1 and 42.0–42.1, respectively. Electron-impact mass spectra show the expected $[M^+ - 2\,ClO_4^-]$ ion peaks.

2,2′-Bis-(1,3,4-thiadiazolium) salt **19** reacts with 2-substituted ethylamines such as ethanolamine, cysteamine and 2-bromoethylamine, in the presence of equimolecular amounts of triethylamine, to give the functionalized 2,2′-bis-(5-ethylimino-4-methyl-1,3,4-thiadiazolines) **22**–**24** in excellent yield (86–91%). Preparation of azide **25** was achieved from bromide **24** and sodium azide in dimethyl sulphoxide (DMSO), in 79% yield. Similarly, the salt **20** reacted with ethanolamine to give diol **26**, and the salt **21** with propylamine and ethanolamine to give products **27** and **28**, respectively, in high yield (Scheme 3).

In order to identify unambiguously the structure and spatial disposition of the rings and side-chains of the reaction products, X-ray structure determination of crystalline compound **22** has been performed. Table 1 presents the main geometrical features (see Fig. 1). Bond distances in the ring agree with the values found from a search in the CSD[10] for such fragments; seven hits were obtained from the four compounds[11-14] with codes BIPTDZ, CIDSOX, GEXVAG and MPTZTD. The angular deformations within the ring follow the pattern found in the aforementioned literature: a planar ring, with the typical bond angle of 88° at the sulphur atom, with almost a pentagonal value at C(2) and N(4), and angles of *ca.* 117° at N(3) and C(5). The centrosymmetric molecular has a conformation similar to that of a fully extended chain (torsion angles either *ca.* 0° or *ca.* 180°), except at the terminal OH group, which is disordered into two (partially occupied) positions. This disorder is peculiar in the sense that it follows a tetrahedral pattern, as the two positions occupied by the OH group correspond to those of the tetrahedron arrangement of C(8) so, although H(8A) is well defined in the difference synthesis, the other hydrogen atom does not appear, hidden by the disordered oxygen atom. In this way, the two oxygen positions form torsion angles of *ca.* $\pm 60°$ with respect to the N(6) nitrogen (Table 1).

As far as the disorder is concerned, we think that the molecules assume a centrosymmetrical configuration with the OH group either at the O(9) or the O(10) position, in a 50:50 ratio. They pack strongly through the O(10)–H(10) interaction, in extended chains, somehow along the ⟨1 0 1⟩ direction. The



Scheme 3 *Reagents and conditions:* i, ClOCCOCl, CH_2Cl_2, 0 °C; ii, terephthaloyl dichloride, toluene, reflux; iii, pyridine-2,6-dicarbonyl dichloride, toluene, reflux; iv, Ac_2O–$HClO_4$, Et_2O, 0 °C to room temp.; v, $H_2N[CH_2]_2X$, Et_3N, EtOH, reflux

Table 1 Selected geometrical parameters (Å, °)

S(1)–C(2)	1.778(3)	S(1)–C(5)	1.749(4)
C(2)–N(3)	1.380(5)	C(2)–N(6)	1.270(4)
N(3)–N(4)	1.357(4)	N(3)–C(11)	1.447(5)
N(4)–C(5)	1.287(5)	C(5)–C(5)^{i}	1.437(4)
N(6)–C(7)	1.456(6)	C(7)–C(8)	1.494(6)
C(8)–O(9)	1.335(7)	C(8)–O(10)	1.217(8)
C(2)–S(1)–C(5)	88.1(2)	S(1)–C(2)–N(6)	128.5(3)
S(1)–C(2)–N(3)	107.6(3)	N(3)–C(2)–N(6)	123.8(3)
C(2)–N(3)–C(11)	123.2(3)	C(2)–N(3)–N(4)	117.2(3)
N(4)–N(3)–C(11)	119.6(3)	N(3)–N(4)–C(5)	111.2(3)
S(1)–C(5)–N(4)	115.9(3)	N(4)–C(5)–C(5)^{i}	122.2(3)
S(1)–C(5)–C(5)^{i}	121.9(3)	C(2)–N(6)–C(7)	116.8(3)
N(6)–C(7)–C(8)	111.4(4)	C(7)–C(8)–O(9)	115.9(5)
C(7)–C(8)–O(19)	118.0(4)		
S(1)–C(2)–N(6)–C(7)	−0.5(5)	N(3)–C(2)–N(6)–C(7)	−179.3(3)
N(6)–C(2)–N(3)–N(4)	179.9(3)	N(3)–N(4)–C(5)–C(5)^{i}	−178.8(3)
C(2)–N(6)–C(7)–C(8)	−175.1(4)	N(6)–C(7)–C(8)–O(9)	58.0(6)
N(6)–C(7)–C(8)–O(10)	−58.5(7)		
O(9) ··· O(10)^{ii}	2.852(9)	O(9)–H(9) ··· O(10)^{ii}	156(−)
O(9) ··· O(10)^{iii}	2.830(8)	O(10)–H(10) ··· O(9)^{iii}	175(12)
H(9) ··· O(10)^{ii}	1.94(−)	H(10) ··· O(9)^{iii}	1.95(12)
O(9)–H(9)	0.97(−)	O(10)–H(10)	1.05(13)

Italics stand for symmetry operation: $i = -x, -y, 1 - z$, $ii = x, y, z - 1$ and $iii = 1 - x, 2 - y, -z$

weaker interaction through H(9) joins chains along *c*, alternating oxygen positions, and closing the interaction circuit around (0.5, 1.0, 0.5). The internal symmetry of the molecule facilitates the positional disorder of the chains (or an inversion twinning), giving rise to the pattern shown in Fig. 2.

The identity of compounds **22**–**28** has also been ascertained by 2D-NMR, HCCOR and DEPT experiments. In the ^1H NMR spectra of compounds **22**–**28**, the *N*-methyl group appears as a singlet at δ 3.36–3.99. For compound **22** the *N*- and *X*-linked methylene groups appear as well resolved signals at δ 3.14 and 3.60, respectively; for **23** they appear as two multiplets centred at δ 3.84 and 3.14, respectively; for dibromide **24** as a complex multiplet centred at δ 3.56; and for diazide **25** as a triplet at δ 3.51 and a broad singlet at δ 3.34, respectively. Salient features of the ^{13}C NMR spectra are given in Table 2. The mass spectra showed the expected molecular ion peak and the

Table 2 ^{13}C δ-Values of 2,2′-Bis-(5-ethylimino-4,5-dihydro-4-methyl-1,3,4-thiadiazoles)

Compound	NMe	XCH_2	$=NCH_2$	C(2)	C(5)	Others
22[a]	35.5	61.1	60.1	135.9	154.3	
23[b]	35.9	46.7	51.7	142.2	166.9	
24[c]	35.9	32.2	59.1	137.0	156.7	
25[c]	35.7	51.8	57.0	136.9	156.7	
26[b]	39.0	59.8	54.4	152.1	169.3	128.2, 131.0
27[d]	35.6	24.1	59.8	145.2	157.1	11.9, 118.5, 136.8, 148.9
28[c]	38.5	66.0	50.0	155.6	170.8	124.2, 140.9, 146.5

[a] In [$^2H_6$]DMSO. [b] In [$^2H_6$]DMSO–TFA. [c] In CDCl. [d] In TFA–$CDCl_3$.

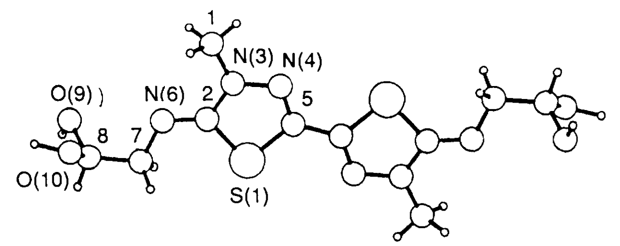


Fig. 1 The molecular structure of the dimeric molecule **22**, showing the atomic numbering used for the crystallographic analysis [15]

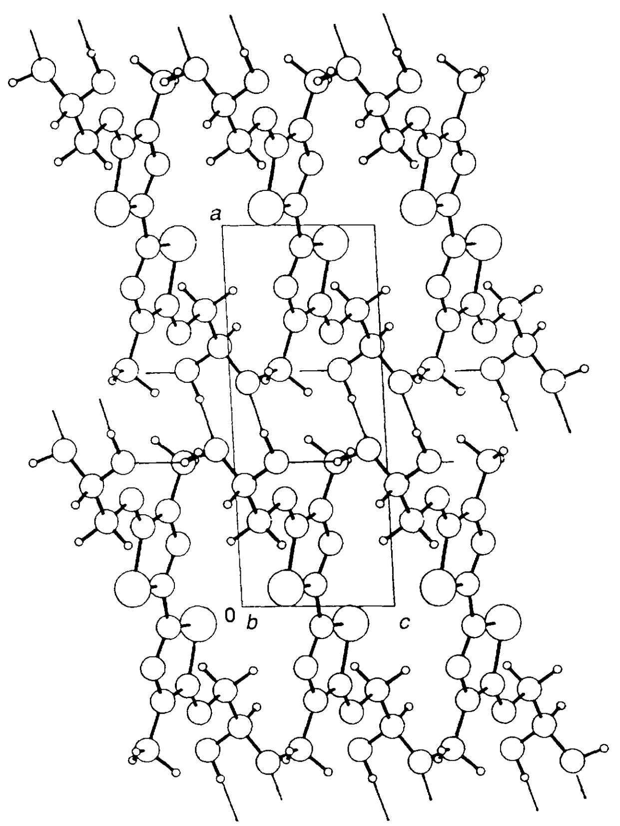


Fig. 2 Crystal packing of the title compound, showing the disordered OH group and the hydrogen interactions

fragmentation pattern was in good agreement with the proposed structures.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Nicolet-FT 5DX spectrometer. ^{1}H NMR data were obtained using a Bruker AC 200 instrument at 200 MHz, with $SiMe_4$ as internal standard. ^{13}C NMR spectra were recorded on a Bruker AC 200 at 50 MHz. *J*-Values are in Hz. Electron-impact mass spectra were run on a Hewlett Packard 5993 C spectrometer at an ionization potential of 70 eV. Elemental analyses were performed with a Perkin-Elmer 240 C instrument. TFA is trifluoroacetic acid.

4-Methyl-5-methylthio-1,3,4-thiadiazolium-2-thiolate **3**.—A suspension of methyl 2-methyl-3-(triphenylphosphoranylidene)dithiocarbazate **2** (19.83 g, 50 mmol) in carbon disulphide (100 cm^3) was vigorously stirred at room temperature for 8 h. The solvent was removed under reduced pressure and the resulting solid was triturated with diethyl ether (50 cm^3), filtered, washed with diethyl ether (4 × 20 cm^3) and recrystallized from chloroform to give the title compound in 81% yield, as yellow prisms, m.p. 141 °C (Found: C, 27.0; H, 3.4; N, 15.7. Calc. for $C_4H_6N_2S_3$: C, 26.95; H, 3.4; N, 15.7%); ν_{max}(Nujol)/cm^{-1} 1491, 1464, 1425, 1362, 1324, 1253, 1111, 1004, 990, 927 and 648; δ_H([$^2H_6$]DMSO) 3.79 (3 H, s, MeN) and 2.82 (3 H, s, MeS); δ_C([$^2H_6$]DMSO; GATEDEC) 181.0 (s, C-2), 167.8 (m, C-5), 40.6 (q, ^1J 144.4, MeN) and 19.6 (q, ^1J 144.4, MeS); *m/z* (%) 178 (M$^+$, 100), 164 (7), 105 (43), 102 (22), 91 (27), 88 (5), 87 (5), 76 (31), 74 (16), 73 (33), 72 (58), 59 (26) and 47 (27).

General Procedure for the Preparation of 5-Alkylthio-3-methyl-1,3,4-thiadiazoline-2-thiones **4** *and* **5**.—To a solution of 4-methyl-5-methylthio-1,3,4-thiadiazolium-2-thiolate **3** (1.40 g, 5 mmol) in chloroform (35 cm^3) was added the corresponding alkyl halide (5.25 mmol). The solution was refluxed for 6 h and, on cooling, the solvent was removed under reduced pressure. The resulting material was triturated with diethyl ether (20 cm^3), filtered off and recrystallized from ethanol. 3-Methyl-5-methylthio-1,3,4-thiadiazol-2(3*H*)-thione **4** (93%) was obtained as yellow needles, m.p. 84 °C (lit.,[1] 81–82 °C); ν_{max}(Nujol)/cm^{-1} 1462, 1429, 1360, 1310, 1258, 1150, 1123, 1061, 1007, 974, 909 and 702; δ_C($CDCl_3$; GATEDEC) 185.0 (q, $^3J_{CNCH}$ 5.3, C-2), 156.2 (q, $^3J_{CSCH}$ 3.4, C-5), 38.6 (q, ^1J 142.7, MeN) and 15.4 (q, ^1J 143.1, MeS); *m/z* (%) 178 (M$^+$, 100), 164 (10), 132 (5), 105 (23), 102 (11), 91 (18), 88 (5), 87 (4), 76 (26), 73 (18), 72 (33) and 59 (17). *5-Benzylthio-3-methyl-1,3,4-thiadiazol-2(3H)-thione* **5** (89%) was obtained as yellow prisms, m.p. 77 °C (Found: C, 47.3; H, 4.0; N, 11.1. Calc. for $C_{10}H_{10}N_2S_3$: C, 47.2; H, 4.0; N, 11.0%); ν_{max}(Nujol)/cm^{-1} 1495, 1472, 1454, 1350, 1263, 1126, 1051, 906, 777, 715 and 701; δ_H($CDCl_3$) 7.35–7.33 (5 H, m), 4.30 (2 H, s, CH_2S) and 3.83 (3 H, s, MeN); δ_C($CDCl_3$; GATEDEC) 185.4 (q, $^3J_{CNCH}$ 3.4, C-2), 154.6 (t, $^3J_{CSCH}$ 4.8, C-5), 134.9 (m), 128.7 (dm), 128.1 (dtt, ^1J 161.4, ^3J 6.4, ^3J 1.7), 38.7 (q, ^1J 142.8, MeN) and 37.7 (tm, ^1J 144.0, CH_2S); *m/z* (%) 254 (M$^+$, 13), 163 (2), 149 (3), 121 (4), 105 (2), 91 (100), 87 (6), 77 (7), 76 (14) and 73 (7).

3-Methyl-2,5-bis(methylthio)-1,3,4-thiadiazolium Tetrafluoroborate **6**.—*Method A*. To a solution of 3-methyl-5-methylthio-1,3,4-thiadiazol-2(3*H*)-thione **4** (0.53 g, 3 mmol) in dry methylene dichloride (20 cm^3) was added trimethyloxonium tetrafluoroborate (0.47 g, 3.15 mmol), and the mixture was stirred under reflux for 3 h. On cooling, the separated crystals were collected by filtration and recrystallized from dry chloroform (94%).

Method B. To a solution of 4-methyl-5-methylthio-1,3,4-thiadiazolium-2-thiolate **3** (0.53 g, 3 mmol) in dry methylene dichloride (20 cm^3) was added trimethyloxonium tetrafluoroborate (0.47 g, 3.15 mmol). The reaction mixture was refluxed for 4 h and, on cooling, the crystals formed were separated and recrystallized from dry chloroform, to give the title compound as prisms in 92% yield, m.p. 76 °C (Found: C, 21.4; H, 3.3; N, 10.0. Calc. for $C_5H_9BF_4N_2S_3$: C, 21.4; H, 3.2; N, 10.0%); ν_{max}(Nujol)/cm^{-1} 1499, 1457, 1430, 1394, 1322, 1270, 1126, 1097, 1061, 992, 966, 935 and 703; δ_H($CDCl_3$–[^{2}H]TFA) 4.09 (3 H, s, MeN), 2.99 (3 H, s, 2-SMe) and 2.78 (3 H, s, 5-SMe); δ_C($CDCl_3$–CF_3CO_2D) 178.3 (C-2), 167.9 (C-5), 41.7 (MeN), 20.3 (2-SMe) and 16.5 (5-SMe); *m/z* (%) 193 ($M^+ - BF_4^-$, 20), 178 (100), 105 (18), 102 (11), 91 (10), 76 (11), 74 (6), 73 (13) and 72 (19).

General Procedure for the Preparation of 5,5′-*Ylenedithiobis*-(3-*methyl*-1,3,4-*thiadiazoline-2-thiones*) **7**–**9**.—To a solution of 4-methyl-5-methylthio-1,3,4-thiadiazolium-2-thiolate **3** (1.40 g, 5 mmol) in chloroform (35 cm^3) was added the corresponding α,ω-dihalogeno derivative (2.5 mmol). The solution was stirred at reflux temperature for 6 h and the solvent was evaporated off under reduced pressure. The resulting material was scratched with diethyl ether (20 cm^3), filtered off, washed with diethyl ether (2 × 15 cm^3) and recrystallized from ethanol. 5,5′-*Tetramethylenedithiobis*-[3-*methyl*-1,3,4-*thiadiazol*-2(3H)-*thione*] **7** (92%) was obtained as prisms, m.p. 118–119 °C (Found: C, 31.5; H, 3.6; N, 14.7. Calc. for $C_{10}H_{14}N_4S_6$: C, 31.4; H, 3.7; N, 14.6%); ν_{max}(Nujol)/cm^{-1} 1468, 1412, 1358, 1261, 1125, 1049, 1002, 906, 723 and 710; δ_H([$^2H_6$]DMSO) 3.78 (3 H, s, MeN), 3.21 (2 H, t, *J* 6.15, CH_2S) and 1.81 (2 H, m, CH_2CH_2S); δ_C([$^2H_6$]DMSO) 184.4 (C-2), 155.1 (C-5), 38.6 (MeN), 32.4 (CH_2S) and 27.3 (CH_2CH_2S); *m/z* (%) 382 (M^+, 2), 299 (18), 297 (17), 276 (15), 219 (32), 204 (18), 178 (10), 177 (100), 163 (16), 149 (22), 147 (5), 143 (6), 129 (9), 120 (8), 105 (55), 104 (41), 102 (19), 91 (12), 90 (11), 88 (19), 87 (12), 83 (15), 76 (22), 73 (30) and 55 (44).

5,5′-[(*Z*)-*But*-2-*enylenedithio*]*bis*-[3-*methyl*-1,3,4-*thiadiazole*-2(3H)-*thione*] **8** (74%) was obtained as needles, m.p. 110–111 °C (Found: C, 31.45; H, 3.2; N, 14.8. Calc. for $C_{10}H_{12}N_4S_6$: C, 31.6; H, 3.2; N, 14.7%); ν_{max}(Nujol)/cm^{-1} 1464, 1425, 1352, 1255, 1118, 1043, 1003, 900, 800, 725 and 704; δ_H($CDCl_3$) 5.80 (1 H, dtd, *J* 8.99, 6.60, *J* 1.49, =CH), 3.87 (2 H, dd, *J* 6.43, 1.49, CH_2) and 3.85 (3 H, s, MeN); δ_C($CDCl_3$) 185.4 (C-2), 153.8 (C-5), 127.7 (=CH), 38.7 (MeN) and 29.8 (CH_2S); *m/z* (%) 380 (M^+, 19), 219 (15), 217 (77), 206 (65), 201 (14), 164 (100), 163 (92), 146 (46), 145 (34), 141 (33), 131 (32), 118 (24), 105 (50), 91 (24), 87 (98), 86 (29), 85 (66), 76 (35), 73 (72), 72 (65), 59 (30), 58 (33) and 55 (26).

5,5′-(o-*Xylidenedithio*)*bis*-[3-*methyl*-1,3,4-*thiadiazole*-2(3H)-*thione*] **9** (73%) was obtained as prisms, m.p. 112–113 °C (Found: C, 39.0; H, 3.2; N, 12.9. Calc. for $C_{14}H_{14}N_4S_6$: C, 39.05; H, 3.3; N, 13.0%); ν_{max}(Nujol)/cm^{-1} 1466, 1423, 1352, 1261, 1122, 1051, 1008, 902, 868, 846, 783, 767, 707 and 690; δ_H($CDCl_3$–TFA) 7.43–7.30 (4 H, m), 4.50 (4 H, s, CH_2S) and 3.87 (6 H, s, MeN); δ_C($CDCl_3$–TFA) 185.6 (C-2), 155.5 (C-5), 133.5, 131.5, 129.4, 39.2 (MeN) and 35.3 (CH_2S); *m/z* (%) 430 (M^+, 7), 267 (4), 219 (3), 191 (12), 164 (12), 162 (8), 136 (30), 135 (100), 134 (11), 131 (11), 105 (19), 104 (29), 91 (23), 77 (15), 76 (7), 73 (22) and 58 (15).

5,5′-*Tetramethylenedithiobis*-(3-*methyl*-2-*methylthio*-1,3,4-*thiadiazolium*) *Bistetrafluoroborate* **10**.—To a solution of 5,5′-tetramethylenedithiobis-[3-methyl-1,3,4-thiadiazole-2(3*H*)-thione] **7** (0.57 g, 1.5 mmol) in dry methylene dichloride (20 cm^3) was added trimethyloxonium tetrafluoroborate (0.47 g, 3.15 mmol), and the resulting mixture was refluxed for 6 h. On cooling, the crystals formed were collected by filtration and recrystallized from methylene dichloride to give the title compound **10** in 69% yield as prisms, m.p. 158–159 °C (Found: C, 24.7; H, 3.3; N, 9.5. Calc. for $C_{12}H_{20}B_2F_8N_4S_6$: C, 24.6; H, 3.4; N, 9.6%); ν_{max}(Nujol)/cm^{-1} 1491, 1462, 1413, 1280, 1060, 941, 862, 771 and 706; δ_H([$^2H_6$]DMSO) 4.02 (6 H, s, MeN), 3.37 (4 H, t, *J* 6.1, CH_2S), 2.96 (6 H, s, MeS) and 1.86 (4 H, t, *J* 6.1, CH_2CH_2S); *m/z* (%) 412 ($M^+ - 2\ BF_4^-$, 2), 382 (5), 277 (4), 218 (15), 203 (3), 193 (3), 178 (100), 164 (24), 114 (13), 105 (82), 102 (24), 91 (31), 76 (34), 73 (43), 72 (80), 59 (32) and 55 (31).

General Procedure for the Preparation of Compounds **11**–**14**.—To a solution of 4-methyl-5-methylthio-1,3,4-thiadiazolium-2-thiolate **3** (0.71 g, 4 mmol) in chloroform (40 cm^3) were added the appropriate α,ω-diamino derivative (4 mmol) and triethylamine (0.4 g, 4 mmol). The mixture was stirred at reflux temperature for 6 h and the resulting solid was filtered off and recrystallized from the appropriate solvent to yield compounds **11** and **12** or **13** and **14**, depending on the chain length of the diamino derivative used (Method A). Compound **12** was also prepared by reaction of 2,2′-tetramethylenediiminobis-(2,3-dihydro-3-methyl-5-methylthio-1,3,4-thiadiazole) **15** (0.75 g, 2 mmol) with tetramethylenediamine (0.22 g, 25 mmol) in ethanol (20 cm^3) at reflux for 24 h, followed by the work-up previously described.

[5,5′]*Ethylenediamino*[2,2′]*ethylenediiminobis*-(2,3-*dihydro*-3-*methyl*-1,3,4-*thiadiazolo*)*phane* **11** (58%) was obtained as prisms, m.p. 250 °C (from propan-1-ol) (Found: C, 38.5; H, 5.3; N, 35.7. Calc. for $C_{10}H_{16}N_8S_2$: C, 38.45; H, 5.2; N, 35.9%); ν_{max}(Nujol)/cm^{-1} 1653, 1568, 1449, 1400, 1354, 1302, 1172, 1128, 1078, 1068, 1035, 1005, 929 and 692; δ_H($CDCl_3$–TFA) 8.63 (1 H, br s, NH), 4.05–3.85 (5 H, m) and 3.66 (2 H, q, *J* 5.14, CH_2NH); δ_C($CDCl_3$–TFA) 169.8 (C-2), 161.4 (C-5), 47.9 (CH_2N), 39.1 (CH_2NH) and 37.1 (MeN); *m/z* (%) 312 (M^+, 1), 286 (6), 173 (82), 156 (17), 140 (21), 114 (87), 102 (40), 99 (50), 98 (20), 88 (21), 87 (20), 86 (100), 85 (17), 84 (10), 73 (13), 72 (26), 70 (24) and 69 (90).

[5,5′]*Tetramethylenediamino*[2,2′]*tetramethylenediiminobis*-(2,3-*dihydro*-3-*methyl*-1,3,4-*thiadiazolo*)*phane* **12** (78%, Method A, and 75%, Method B) was obtained as prisms, m.p. 166 °C (from EtOH) (Found: C, 45.8; H, 6.5; N, 30.5. Calc. for $C_{14}H_{24}N_8S_2$: C, 45.6; H, 6.6; N, 30.4%); ν_{max}(Nujol)/cm^{-1} 3369, 1626, 1568, 1462, 1404, 1375, 1338, 1255, 1143, 1068, 1018, 1001, 932 and 711; δ_H([$^2H_6$]DMSO) 3.92 (1 H, br s, NH), 3.20 (3 H, s, MeN), 2.90 (2 H, t, *J* 5.78, CH_2N), 2.82 (2 H, t, *J* 6.79, CH_2NH) and 1.66–1.53 (4 H, m); δ_C([$^2H_6$]DMSO) 162.0 (C-2), 159.2 (C-5), 55.3 (CH_2N), 39.0 (CH_2NH), 34.4 (MeN), 27.9 and 25.7; *m/z* (%) 241 (2), 227 (16), 199 (52), 185 (100), 184 (3), 173 (48), 170 (12), 168 (42), 160 (14), 130 (44), 128 (9), 116 (12), 114 (19), 102 (31), 100 (7), 88 (23), 86 (20), 85 (14), 73 (21), 72 (55) and 70 (85).

5,5′-*Hexamethylenediiminobis*-(4,5-*dihydro*-4-*methyl*-1,3,4-*thiadiazole*-2-*thiol*) **13** (78%) was obtained as prisms, m.p. 171–173 °C (from EtOH) (Found: C, 38.4; H, 5.4; N, 22.2. Calc. for $C_{12}H_{20}N_6S_4$: C, 38.3; H, 5.35; N, 22.3%); ν_{max}(Nujol)/cm^{-1} 1609, 1457, 1432, 1417, 1289, 1239, 1191, 1092, 990, 934 and 638; δ_H([$^2H_6$]DMSO) 3.49 (3 H, s, MeN), 3.14 (2 H, br s, CH_2N), 1.56 (2 H, br s, CH_2CH_2N) and 1.32 (2 H, br s, $CH_2CH_2CH_2N$); δ_C([$^2H_6$]DMSO) 167.8 (C-2), 165.3 (C-5), 49.7 (CH_2N), 36.5 (MeN), 28.2 (CH_2CH_2N) and 25.5 ($CH_2CH_2CH_2N$); *m/z* (%) 376 (M^+, 88), 375 (6), 343 (27), 230 (17), 216 (17), 196 (44), 188 (17), 174 (12), 161 (16), 151 (14), 148 (100), 147 (75), 146 (25), 139 (11), 128 (12), 116 (10), 111 (12), 102 (13), 97 (13), 87 (11), 83 (16), 73 (12), 72 (16) and 69 (31).

5,5′-*Octamethylenediiminobis*-(4,5-*dihydro*-4-*methyl*-1,3,4-*thiadiazole*-2-*thiol*) **14** (81%) was obtained as prisms, m.p. 164 °C (from EtOH) (Found: C, 41.6; H, 6.05; N, 20.75. Calc. for $C_{14}H_{24}N_6S_4$: 41.6; H, 6.0; N, 20.8%); ν_{max}(Nujol)/cm^{-1} 1603, 1431, 1412, 1230, 1109, 992, 932 and 722; δ_H([$^2H_6$]DMSO) 9.84 (1 H, br s, NH), 3.61 (3 H, s, MeN), 3.13 (2 H, t, *J* 6.88,

CH_2N), 1.58 (2 H, br s, CH_2CH_2N) and 1.28 (4 H, s, $CH_2CH_2CH_2CH_2N$); δ_C([$^2H_6$]DMSO) 168.0 (C-2), 165.5 (C-5), 49.5 (CH_2N), 37.3 (MeN), 28.5 ($CH_2CH_2CH_2CH_2N$), 28.1 (CH_2CH_2N) and 25.9 ($CH_2CH_2CH_2N$); *m/z* (%) 404 (M^+, 21), 403 (32), 371 (6), 180 (13), 178 (100), 164 (13), 148 (85), 147 (51), 139 (25), 129 (11), 111 (10), 102 (10), 97 (8), 87 (7), 83 (5), 73 (12) and 72 (17).

2,2'-*Tetramethylenediiminobis-(2,3-dihydro-3-methyl-5-methylthio-1,3,4-thiadiazole)* **15**.—To a solution of 4-methyl-5-methylthio-1,3,4-thiadiazolium-2-thiolate **3** (1.40 g, 5 mmol) in methylene dichloride (35 cm^3) were added tetramethylenediamine (0.22 g, 2.5 mmol), triethylamine (0.51 g, 5 mmol) and methyl iodide (2.13 g, 15 mmol). The reaction mixture was refluxed for 3 h, the solvent was removed under reduced pressure and the resulting material was triturated with cold ethanol (10 cm^3). The solid formed was filtered off and recrystallized from ethanol to give the title compound in 53% yield, as yellow prisms, m.p. 198–199 °C (Found: C, 38.3; H, 5.4; N, 22.2. Calc. for $C_{12}H_{20}N_6S_4$: C, 38.3; H, 5.35; N, 22.3%); ν_{max}(Nujol)/cm^{-1} 1606, 1494, 1460, 1419, 1346, 1319, 1300, 1250, 1197, 1072, 972, 945, 916, 758, 707 and 700; δ_H([$^2H_6$]DMSO) 3.86 (3 H, s, MeN), 3.34 (2 H, br s, CH_2N), 2.67 (3 H, s, MeS) and 1.79 (2 H, br s, CH_2CH_2N); δ_C([$^2H_6$]DMSO) 166.1 (C-2), 152.0 (C-5), 50.7 (CH_2N), 38.5 (MeN), 24.8 (CH_2CH_2N) and 16.1 (MeS); *m/z* (%) 376 (M^+, 9), 343 (28), 329 (5), 270 (15), 229 (3), 216 (7), 214 (11), 202 (5), 200 (5), 188 (11), 174 (29), 168 (6), 161 (12), 156 (6), 147 (17), 142 (19), 128 (100), 127 (67), 116 (9), 102 (14), 91 (10), 82 (3), 74 (9), 73 (7), 72 (8) and 69 (22).

Dimethyl 3,3'-*Oxalylbis-(2-methyldithiocarbazate)* **16**.—To a solution of methyl 2-methyldithiocarbazate **1** (0.41 g, 3 mmol) in dry methylene dichloride (30 cm^3) at 0 °C, was added oxalyl dichloride (0.42 g, 3.3 mmol) and the resulting suspension was kept at room temperature for 2 h. The solid formed was collected by filtration and crystallized from ethanol to give the title compound in 94% yield, as yellow needles, m.p. 255 °C (Found: C, 29.5; H, 4.2; N, 17.1. Calc. for $C_8H_{14}N_4O_2S_4$: C, 29.4; H, 4.3; N, 17.2%); ν_{max}(Nujol)/cm^{-1} 3268, 1700, 1481, 1464, 1377, 1356, 1265, 1167, 1118, 1024, 960, 827 and 721; δ_H([$^2H_6$]DMSO) 12.08 (1 H, s, NH), 3.57 (3 H, s, MeN) and 2.45 (3 H, s, MeS); δ_C([$^2H_6$]DMSO) 201.2 (C=S), 156.6 (C=O), 42.9 (MeN) and 19.1 (MeS); *m/z* (%) 326 (M^+, 3), 278 (2), 230 (3), 163 (98), 115 (31), 91 (100), 76 (7), 74 (20), 73 (28), 47 (16) and 46 (8).

General Procedure for the Preparation of Dimethyl 3,3'-*Arenediyldicarbonylbis-(2-methyldithiocarbazates)* **17** *and* **18**.—To a vigorously stirred solution of methyl 2-methyldithiocarbazate **1** (2.04 g, 15 mmol) in toluene (30 cm^3) was added the corresponding diacyl chloride (7.5 mmol), and the resulting suspension was stirred at reflux temperature for 4 h. After cooling, the solid formed was separated by filtration, washed successively with water (7 cm^3) and diethyl ether (7 cm^3) and crystallized from ethanol.

Dimethyl 3,3'-*terephthaloylbis-(2-methyldithiocarbazate)* **17** (98%) was obtained as prisms, m.p. 341 °C (Found: C, 41.8; H, 4.6; N, 13.9. Calc. for $C_{14}H_{18}N_4O_2S_4$: C, 41.8; H, 4.5; N, 13.9%); ν_{max}(Nujol)/cm^{-1} 3269, 1662, 1525, 1498, 1464, 1354, 1278, 1116, 1047, 964, 860 and 727; δ_H([$^2H_6$]DMSO) 11.82 (2 H, s, NH), 8.06 (4 H, s), 3.68 (6 H, s, MeN) and 2.47 (6 H, s, MeS); δ_C([$^2H_6$]DMSO) 201.5 (C=S), 163.7 (C=O), 134.7, 127.9, 43.4 (MeN) and 18.9 (MeS); *m/z* (%) 402 (M^+, 2), 354 (9), 308 (12), 307 (35), 306 (94), 246 (13), 220 (13), 219 (100), 218 (10), 217 (52), 191 (8), 157 (40), 146 (12), 130 (14), 129 (32), 102 (18), 91 (31), 76 (9), 48 (25) and 47 (30).

Dimethyl 3,3'-*(Pyridine-2,6-dicarbonyl)bis(2-methyldithiocarbazate)* **18** (86%) was obtained as flakes, m.p. 138–140 °C (Found: C, 38.5; H, 4.4; N, 17.3. Calc. for $C_{13}H_{17}N_5O_2S_4$: C, 38.7; H, 4.25; N, 17.35%); ν_{max}(Nujol)/cm^{-1} 3412, 3167, 1682, 1505, 1456, 1360, 1315, 1263, 1231, 1145, 1106, 1084, 1036, 1003, 964, 901, 872, 843, 738 and 680; δ_H([$^2H_6$]DMSO) 12.12 (2 H, s, NH), 8.37 (3 H, br s), 3.75 (6 H, s, MeN) and 2.48 (6 H, s, MeS); δ_C([$^2H_6$]DMSO) 201.9 (C=S), 160.8 (pyridine C-2), 146.7 (C=O), 140.6 (pyridine C-4), 126.1 (pyridine C-3), 43.7 (MeN) and 19.1 (MeS); *m/z* (%) 403 (M^+, 8), 356 (8), 308 (12), 264 (2), 237 (4), 193 (7), 163 (2), 135 (2), 120 (3), 105 (10), 103 (4), 91 (100), 77 (13), 76 (6), 73 (7) and 47 (12).

General Procedure for the Preparation of 2,2'-*Bis-(4-methyl-5-methylthio-1,3,4-thiadiazolium) Diperchlorates* **19**–**21**.—To a suspension of the appropriate dimethyl 3,3'-diacylbis-(2-methyldithiocarbazate) **16**–**18** (2.5 mmol) in dry diethyl ether (15 cm^3)–acetic anhydride (10 cm^3) at 0 °C was added 70% perchloric acid (0.52 cm^3, 6 mmol). Thereafter, the reaction mixture was kept at room temperature for 48 h while being vigorously stirred. The solid formed was filtered off, washed with diethyl ether (2 × 10 cm^3), dried and crystallized from a suitable solvent.

2,2'-*Bis-(4-methyl-5-methylthio-1,3,4-thiadiazolium) diperchlorate* **19** (87%) was obtained as prisms, m.p. 288 °C (from MeCN) (Found: C, 19.5; H, 2.5; N, 11.3. Calc. for $C_8H_{12}Cl_2N_4O_8S_4$: C, 19.6; H, 2.5; N, 11.4%); ν_{max}(Nujol)/cm^{-1} 1489, 1457, 1426, 1385, 1283, 1141, 1094, 1019, 958, 870, 700 and 625; δ_H([$^2H_6$]DMSO) 4.23 (3 H, s, MeN) and 3.20 (3 H, s, MeS); *m/z* (%) 292 ($M^+ - 2\ ClO_4^-$, 2), 262 (5), 131 (2), 110 (12), 105 (36), 91 (4), 76 (28), 74 (10), 73 (100), 58 (23), 52 (57), 47 (27) and 46 (40).

2,2'-(p-*Phenylene)bis-(4-methyl-5-methylthio-1,3,4-thiadiazolium) diperchlorate* **20** (91%) was obtained as prisms, m.p. 320 °C (from MeCN) (Found: C, 29.7; H, 2.8; N, 9.9. Calc. for $C_{14}H_{16}Cl_2N_4O_8S_4$: C, 29.6; H, 2.8; N, 9.9%); ν_{max}(Nujol)/cm^{-1} 1496, 1466, 1406, 1304, 1294, 1093, 922, 848, 721 and 624; δ_H([$^2H_6$]DMSO) 8.26 (4 H, s), 4.23 (6 H, s, MeN) and 3.15 (6 H, s, MeS); δ_C([$^2H_6$]DMSO) 180.3 (C-5), 163.4 (C-2), 130.1, 128.8, 42.1 (MeN) and 21.1 (MeS); *m/z* (%) 368 ($M^+ - 2\ ClO_4^-$, 1), 338 (29), 322 (23), 306 (13), 262 (4), 233 (64), 218 (37), 217 (100), 186 (5), 157 (71), 156 (33), 146 (36), 130 (30), 129 (82), 128 (55), 120 (11), 102 (20), 76 (24), 73 (75), 72 (84) and 48 (48).

2,2'-*(Pyridine-2,6-diyl)bis-(4-methyl-5-methylthio-1,3,4-thiadiazolium) diperchlorate* **21** (87%) was obtained as prisms, m.p. 308 °C [from EtOH–MeCN (1:2)] (Found: C, 27.3; H, 2.8; N, 12.2. Calc. for $C_{13}H_{15}Cl_2N_5O_8S_4$: C, 27.5; H, 2.7; N, 12.3%); ν_{max}(Nujol)/cm^{-1} 1466, 1457, 1436, 1335, 1283, 1136, 1096, 1032, 994, 918, 823, 783, 647 and 624; δ_H($CDCl_3$–TFA) 8.45–8.38 (2 H, m), 8.26 (1 H, dd, *J* 8.83, 6.67), 4.26 (6 H, s, MeN) and 3.16 (6 H, s, MeS); δ_C($CDCl_3$–TFA) 182.7 (C-5), 165.6 (C-2), 145.7 (pyridine C-2), 141.0 (pyridine C-4), 124.8 (pyridine C-3), 42.0 (MeN) and 20.6 (MeS); *m/z* (%) 369 ($M^+ - 2\ ClO_4^-$, 3), 339 (12), 307 (25), 234 (27), 219 (38), 218 (57), 158 (83), 157 (34), 135 (6), 130 (95), 129 (37), 105 (37), 103 (100), 91 (8), 76 (59) and 73 (86).

General Procedure for the Preparation of 2,2'-*Bis-(5-ethylimino-4,5-dihydro-4-methyl-1,3,4-thiadiazoles)* **22**–**24** *and* **26**–**28**.—To a suspension of the appropriate 2,2'-bis-(4-methyl-5-methylthio-1,3,4-thiadiazolium) diperchlorate **19**–**21** (5 mmol) in dry ethanol (40 cm^3) were added triethylamine (1.01 g, 10 mmol) and the corresponding amino derivative (10 mmol) and the reaction mixture was stirred at reflux temperature for 6 h. The resulting solid was filtered off, washed successively with water (2 × 10 cm^3) and diethyl ether (10 cm^3) and crystallized from the appropriate solvent.

2,2'-*Bis-[4,5-dihydro-(2-hydroxyethylimino)-4-methyl-1,3,4-thiadiazole]* **22** (89%) was obtained as yellow prisms, m.p. 227–228 °C (from EtOH) (Found: C, 38.0; H, 5.2; N, 26.45. Calc. for $C_{10}H_{16}N_6O_2S_2$: C, 38.0; H, 5.1; N, 26.6%); ν_{max}(Nujol)/cm^{-1} 3301, 1630, 1612, 1504, 1421, 1325, 1269, 1089, 999, 879, 848 and 725; δ_H([$^2H_6$]DMSO) 4.67 (1 H, t, *J* 5.62, OH), 3.60 (2 H, td, *J* 6.03, 5.62, C*H*$_2$OH), 3.36 (3 H, s, MeN) and 3.14 (2 H, t, *J* 6.03, CH_2N); δ_C([$^2H_6$]DMSO) 154.3 (C-5), 135.9 (C-2), 61.1 (CH_2OH), 60.1 (CH_2N) and 35.5 (MeN); *m/z* (%) 316 (M^+, 17), 285 (100), 214 (45), 195 (60), 182 (78), 171 (66), 154 (34), 153 (87), 127 (91), 110 (12) and 99 (41).

2,2'-*Bis*-[4,5-*dihydro*-5-(2-*mercaptoethylimino*)-4-*methyl*-1,3,4-*thiadiazole*] **23** (86%) was obtained as yellow prisms, m.p. 245–248 °C (from EtOH) (Found: C, 34.5; H, 4.7; N, 24.0. Calc. for $C_{10}H_{16}N_6S_4$: C, 34.5; H, 4.6; N, 24.1%); ν_{max}(Nujol)/cm^{-1} 1634, 1508, 1463, 1321, 1273, 1024, 1005, 986, 856 and 710; δ_H([$^2H_6$]DMSO–[$^2H_6$]TFA) 3.94 (3 H, s, MeN), 3.88–3.80 (2 H, m, CH_2N), 3.20–3.09 (2 H, m, CH_2S) and 1.24 (1 H, t, *J* 7.29, SH); δ_C([$^2H_6$]DMSO–[$^2H_6$]TFA) 166.9 (C-5), 142.2 (C-2), 51.7 (CH_2N), 46.7 (CH_2SH) and 35.9 (MeN); *m/z* (%) 348 (M^+, 3), 315 (3), 301 (9), 288 (10), 241 (30), 228 (18), 200 (16), 174 (23), 169 (25), 143 (8), 142 (100), 119 (40), 116 (44), 115 (28), 114 (25), 110 (28), 88 (31), 87 (27), 86 (26), 73 (42), 72 (50), 61 (32), 60 (63), 59 (65), 55 (44) and 47 (34).

2,2'-*Bis*-[5-(2-*bromoethylimino*)-4,5-*dihydro*-4-*methyl*-1,3,4-*thiadiazole*] **24** (91%) was obtained as yellow prisms, m.p. 172 °C (from EtOH) (Found: C, 27.1; H, 3.3; N, 18.9. Calc. for $C_{10}H_{14}Br_2N_6S_2$: C, 27.2; H, 3.2; N, 19.0%); ν_{max}(Nujol)/cm^{-1} 1614, 1512, 1432, 1358, 1329, 1276, 1214, 1023, 996, 856. 748, 678 and 616; δ_H($CDCl_3$) 3.59 (3 H, s, MeN) and 3.64–3.48 (4 H, m); δ_C($CDCl_3$; GATEDEC) 156.7 (tq, $^3J_{C=NCH}$ 7.42, $^3J_{CNCH}$ 2.04 C-5), 137.0 (s, C-2), 59.1 (dddd, ^1J 138.23, ^1J 135.33, ^2J 4.06, ^2J 2.95, CH_2N), 35.9 (q, ^1J 141.36, MeN) and 32.2 (dddd, ^1J 153.74, ^1J 152.70, ^2J 4.86, ^2J 3.89, CH_2Br); *m/z* (%) 444 (M^+ + 4, 2), 442 (M^+ + 2, 4), 440 (M^+, 2), 439 (11), 362 (3) 360 (3), 349 (14), 348 (100), 347 (13), 346 (93), 276 (2), 274 (2), 182 (63), 153 (41), 127 (58), 113 (6), 110 (26), 109 (12), 108 (11), 99 (32), 82 (10) and 80 (12).

2,2'-(p-*Phenylene*)*bis*-[4,5-*dihydro*-5-(2-*hydroxyethylimino*)-4-*methyl*-1,3,4-*thiadiazole*] **26** (84%) was obtained as yellow prisms, m.p. 247–249 °C (from EtOH) (Found: C, 49.0; H, 5.2; N, 21.4. Calc. for $C_{16}H_{20}N_6O_2S_2$: C, 49.0; H, 5.1; N, 21.4%); ν_{max}(Nujol)/cm^{-1} 3285, 1624, 1462, 1423, 1362, 1341, 1291, 1254, 1090, 1019, 927, 899, 872, 832 and 729; δ_H([$^2H_6$]DMSO–[$^2H_6$]TFA) 8.06 (4 H, s), 3.99 (3 H, s, MeN), 3.79 (2 H, t, *J* 4.32) and 3.60 (2 H, t, *J* 4.32); δ_C([$^2H_6$]DMSO–[$^2H_6$]TFA) 169.2 (C-5), 152.1 (C-2), 131.0, 128.2, 59.8 (CH_2OH), 54.4 (CH_2N) and 39.0 (MeN); *m/z* (%) 392 (M^+, 14). 362 (20), 361 (100), 318 (34), 247 (10), 235 (10), 229 (56), 217 (32), 203 (20), 157 (32), 146 (30), 129 (32), 120 (14), 102 (15), 73 (12) and 72 (12).

2,2'-(*Pyridine*-2,6-*diyl*)*bis*-(4,5-*dihydro*-4-*methyl*-5-*propylimino*-1,3,4-*thiadiazole*) **27** (88%) was obtained as needles, m.p. 150 °C (from EtOH) (Found: C, 52.5; H, 6.15; N, 25.0. Calc. for $C_{17}H_{23}N_7S_2$: C, 52.4; H, 5.95; N, 25.2%); ν_{max}(Nujol)/cm^{-1} 1645, 1634, 1587, 1568, 1532, 1456, 1373, 1344, 1315, 1277, 1157, 1072, 1032, 928, 808, 775, 746, 731 and 642; δ_H($CDCl_3$) 7.85 (1 H, d, *J* 2.01), 7.81 (1 H, s), 7.72 (1 H, dd, *J* 9.04, 6.18), 3.64 (6 H, s, MeN), 3.16 (4 H, t, *J* 7.06, CH_2N), 1.74 (4 H, qt, *J* 7.34, 7.06, C*H*$_2$Me), 1.02 (6 H, t, *J* 7.34, CH_2*Me*); δ_C($CDCl_3$) 157.1 (C-5), 148.9 (pyridine C-2), 145.2 (C-2), 136.8 (pyridine C-4), 118.5 (pyridine C-3), 59.8 (CH_2N), 35.6 (MeN), 24.1 (*C*H$_2$Me) and 11.9 (CH_2*Me*); *m/z* (%) 389 (M^+, 20), 374 (2), 361 (21), 360 (100), 259 (6), 230 (29), 204 (40), 179 (3), 165 (51), 158 (4), 136 (5), 130 (30), 103 (27), 101 (2), 69 (31) and 55 (7).

2,2'-(*Pyridine*-2,6-*diyl*)*bis*-[4,5-*dihydro*-2-*hydroxyethylimino*)-4-*methyl*-1,3,4-*thiadiazole*] **28** (91%) was obtained as needles, m.p. 237 °C (from EtOH) (Found: C, 45.6; H, 4.9; N, 25.1. Calc. for $C_{15}H_{19}N_7O_2S_2$: C, 45.8; H, 4.9; N, 24.9%); ν_{max}(Nujol)/cm^{-1} 3256, 1622, 1603, 1566, 1539, 1456, 1365, 1277, 1096, 1053, 928, 812, 776, 736 and 643; δ_H(TFA–$CDCl_3$) 8.47–8.37 (2 H, m), 8.28 (1 H, dd, *J* 8.97, 6.52), 4.81 (4 H, s) and 4.13 (10 H, s); δ_C(TFA–$CDCl_3$) 170.8 (C-5), 155.6 (C-2), 146.5 (pyridine C-2), 140.9 (pyridine C-4), 124.2 (pyridine C-3), 66.0 (CH_2OH), 50.0 (CH_2N) and 38.5 (MeN); *m/z* (%) 393 (M^+, 7), 363 (19), 362 (100), 277 (5), 262 (4), 259 (5), 248 (12), 230 (89), 205 (12), 204 (99), 186 (9), 165 (82), 162 (17), 157 (15), 149 (18), 147 (44), 135 (16), 132 (7), 130 (75), 121 (12), 115 (27), 103 (64) and 77 (16).

2,2'-*Bis*-[5-(2-*azidoethylimino*)-4,5-*dihydro*-4-*methyl*-1,3,4-*thiadiazole*] **25**.—To a solution of 2,2'-bis-[5-(2-bromoethylimino)-4,5-dihydro-4-methyl-1,3,4-thiadiazole] **24** (0.88 g, 2 mmol) in dry DMSO (30 cm^3) was added sodium azide (0.52 g, 8 mmol), and the reaction mixture was stirred at 70 °C for 12 h. On cooling, the solution was poured into ice–water (100 cm^3), and the solid formed was collected by filtration, washed with water (3 × 15 cm^3), dried and crystallized from hexane to give the title compound in 79% yield, as yellow needles, m.p. 138 °C (Found: C, 32.9; H, 3.7; N, 45.7. Calc. for $C_{10}H_{14}N_{12}S_2$: C, 32.8; H, 3.85; N, 45.9%); ν_{max}(Nujol)/cm^{-1} 2106, 1649, 1462, 1359, 1319, 1275, 1240, 1074, 1033, 1006, 972, 858 and 718; δ_H($CDCl_3$) 3.60 (3 H, s, MeN), 3.51 (2 H, t, *J* 5.29, CH_2N) and 3.34 (2 H, br s, CH_2N_3); δ_C($CDCl_3$) 156.7 (C-5), 136.9 (C-2), 57.0 (CH_2N), 51.8 (CH_2N_3) and 35.7 (MeN); *m/z* (%) 366 (M^+, 13), 338 (4), 310 (65), 282 (3), 269 (6), 255 (2), 241 (5), 214 (4), 187 (7), 182 (18), 171 (30), 159 (3), 154 (18), 153 (100), 141 (6), 128 (12) 127 (54), 114 (2), 88 (5), 87 (3), 86 (4), 73 (16), 72 (10) and 69 (66).

Crystallographic Analysis of 2,2'-*Bis*-[4,5-*dihydro*-5-(2-*hydroxyethylimino*)-4-*methyl*-1,3,4-*thiadiazole*] **22**.—*Crystal data.* $C_{10}H_{16}O_2S_2$, *M* = 316.40, space group *P*1, *a* = 11.286 2(17), *b* = 7.740 9(8), *c* = 4.267 6(2) Å, α = 93.441(5), β = 91.703(6), γ = 108.780(12)°, D_c = 1.493 g cm^{-3}, *Z* = 1. Cell constants obtained from a least-squares fit using 32 reflexions up to θ 45°, Cu-Kα radiation.

Data collection and processing. A transparent yellow prism sample (0.20 × 0.13 × 0.03 mm) was used for the anslysis on a Philips PW1100 diffractometer, with Cu-Kα radiation, graphite monochromator $\omega/2\theta$ scans, bisecting geometry, 1 × 1° detector apertures, 1.6° scan width and using 1 min per reflexion. Good stability for the sample checked every 90 min. of 1104 independent reflexions, up to 75° in θ, 954 were considered observed [$3\sigma(I)$ criterion].

Structure analysis and refinement. The structure was solved by Direct Methods[16] in the *P*1 space group and refined[17] by least-squares procedures for 128 parameters in the *P*1 space group, as refinement in *P*1 did not progress. The OH groups appear to be disordered, population parameter 0.50; the H(9) atom had to be kept fixed in the last cycles of refinement and the H(8B) atom, superimposed on the corresponding O(9) and O(10) positions, could not be located. Empirical absorption correction (μ 34.92 cm^{-1}) was applied,[18] the maximum and minimum transmission factors being 1.370 and 0.597. All the hydrogen atoms but the mentioned H(8B) were located by difference synthesis and they were isotropically included in the last cycles of refinement. An empirical weighting scheme, so as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle|F_o|\rangle$ and $\langle\sin\theta/\lambda\rangle$ was introduced. The final shift/error was 0.02, with maximum peak in the final ΔF of 0.32 e Å^{-3}. The maximum thermal factor was *U*11(010) 0.093(5) Å^2. The final *R*- and R_w-value were 0.049 and 0.050, respectively. All the calculations were performed on a VAX 6410 computer. The atomic scaattering factors were taken from the International Tables.[19] Table 3 shows the final non-hydrogen atomic co-ordinates.*

* *Supplementary Data:* (see Section 5.6.3. of Instructions for Authors, in the January issue). Bond lengths and bond angles, together with their standard deviations and anisotropic thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre.

Table 3 Final atomic co-ordinates

Atom	*x*	*y*	*z*
S(1)	0.0462(1)	0.2679(1)	0.2932(2)
C(2)	0.2095(3)	0.3717(5)	0.3836(8)
N(3)	0.2498(3)	0.2519(4)	0.5500(7)
N(4)	0.1631(3)	0.0897(4)	0.6031(7)
C(5)	0.0543(3)	0.0785(4)	0.4855(7)
N(6)	0.2805(3)	0.5278(4)	0.3175(7)
C(7)	0.2224(4)	0.6381(5)	0.1430(10)
C(8)	0.3175(5)	0.8107(6)	0.0567(12)
*O(9)	0.4116(4)	0.7968(7)	−0.1145(11)
*O(10)	0.3791(7)	0.9110(10)	0.2750(16)
C(11)	0.3780(4)	0.2921(7)	0.6690(12)

Population parameters: $pp(O9) = pp(O10) = 0.5$

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