Reactions of Thiazolidine-2,5-dithiones with Amino Nucleophiles. Synthesis of Imidazolidine-2,4-dithiones, Imidazo[5,1-*a*]-imidazole, -pyrimidine, -perimidine, -[2,1-*b*][1,3,4]thiadiazines and Pyrrole-3(2*H*)-thiones

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Reactions of 4,4-disubstituted thiazolidine-2,5-dithiones with various amino-containing nucleophiles gave 1-substituted imidazolidine-2,4-dithiones **3** and **11**. The diamines, in these reactions, produced fused *N*-containing heterocycles **7a,b** and **10**. Imidazo[2,1-*b*][1,3,4]thiadiazines **14** were synthesized by further reaction of compounds **11** with α-bromoacetophenones. Enamino nitriles reacted as carbanions to give pyrrole-3(2*H*)-thiones **16**.

1,3-Thiazine-2,6-dithiones bearing an electron-withdrawing group, in particular an alkyl- or aryl-sulphonyl or cyano group, at the 5-position were previously shown to react with various nucleophiles and amino-containing nucleophiles to give fused heterocycles, such as pyrimidines, thiadiazines, thiopyridones, reductively alkylated thiazinethiones and dithiocinnamic acid derivatives by ring-opening reactions of thiazinedithiones.[1]

A series of thiazolidine-2,5-dithiones corresponding to the ring-contracted compounds of 1,3-thiazine-2,6-dithiones were initially synthesized.[2] Abnormal methylation reactions and marked susceptibility to oxidation to give bis(dihydrothiazol-5-yl) disulphides also occurred in the case of thiazolidinedithiones having a hydrogen at the 4-position. MNDO molecular orbital calculations adequately explained these methylations and oxidations of 4-monosubstituted thiazolidinedithiones.[2]

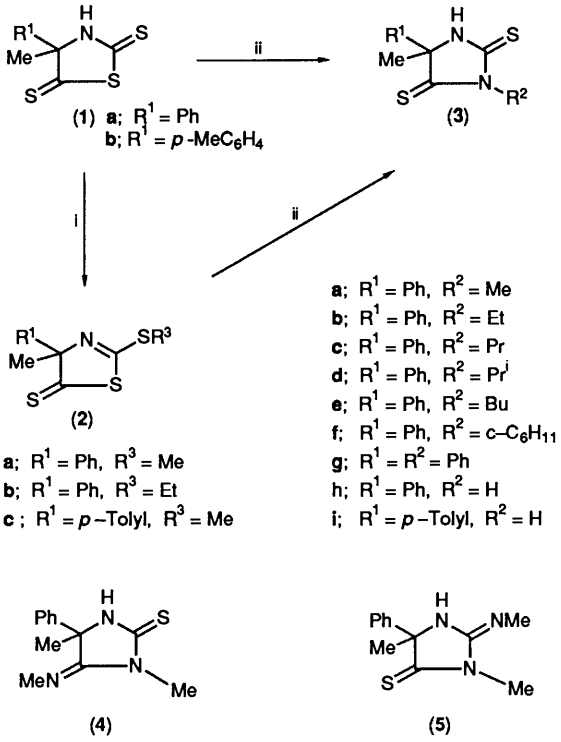
No reports appear to be available on the reactions of thiazolidine-2,5-dithiones with electrophiles and nucleophiles. The present study was conducted in order to examine the reactions of thiazolidine-2,5-dithiones with amino-containing nucleophiles such as amines, diamines, hydrazines, enamino nitriles and thiourea, leading to the formation of imidazolidine-2,4-dithiones, imidazo-[5,1-*a*]imidazole, -pyrimidine, -perimidine, -[2,1-*b*][1,3,4]thiadiazines and pyrrole-3(2*H*)-thiones. The reaction mechanisms involved are briefly discussed based on the results of reactions of 4,4-disubstituted thiazolidinedithiones with the nucleophiles used.

4-Methyl-4-phenylthiazolidine-2,5-dithione **1a** when added to an excess of a primary amine in 50% ethanol followed by warming to obtain a clear solution and then storage at room temperature, gave 3-substituted 5-methyl-5-phenylimidazolidine-2,4-dithiones **3** in moderate to high yield except for **3g** (45%) produced by reaction with aniline. Only methylamine, when used in large excess, yielded the 1-methyl-5-methyliminoimidazolidine-2-thione **4** as the major product along with compound **3a**. The latter was obtained as the sole product in quantitative yield when normal excess of methylamine (2.5 mol equiv.) reacted with the reactant under the same reaction conditions.

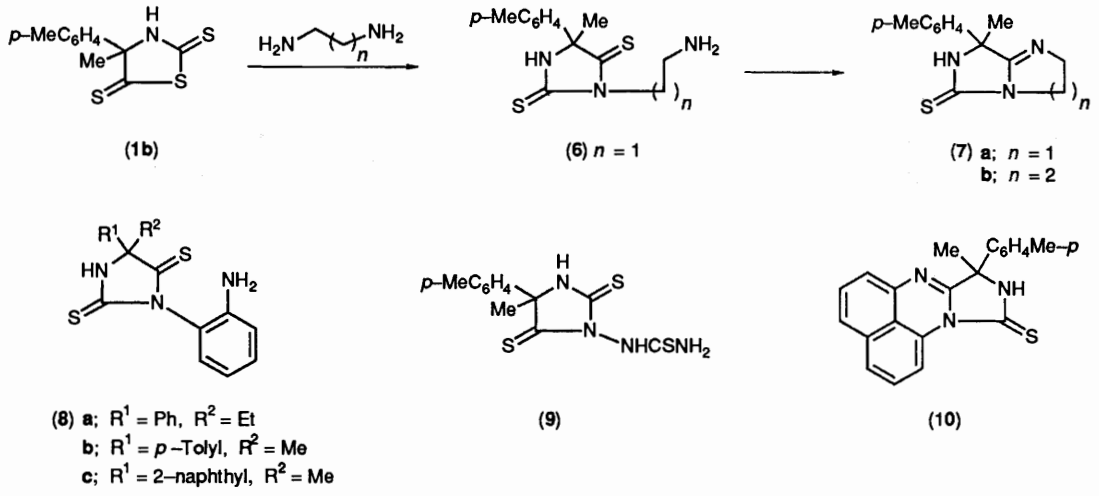
Compounds **3** were also synthesized in quantitative yields on treatment of 2-alkylthiothiazol-5(4*H*)-thiones **2** with alkylamines in EtOH. Compounds **2** were easily produced by reaction of thiazolidinedithiones with alkyl iodides (Scheme 1).

The structural isomer of compound **4**, 3-methyl-2-methyliminothiazolidine-4-thione **5** or its tautomer, could not be obtained. The structure of compound **4** was easily determined from its ^{13}C NMR spectrum and from that of thiazolidinedithione (see Experimental section). Amines higher than methylamine failed to give compounds homologous to compound **4**, whereas 1, ω-alkylene diamines and naphthalene-1,8-diamine reacted quite smoothly with thiazolidinedithiones to form fused *N*-containing heterocycles **7** and **10**, corresponding to compound **4**, in good yield (Scheme 2). The intermediate, the 3-(2-aminoethyl)imidazolidine-2,4-dithione **6**, was isolated after a short reaction period. *o*-Phenylenediamine also gave intermediate compounds **8a–c** in high yield. However, in no case could these intermediates **8a–c** be converted into fused *N*-containing heterocycles corresponding to compounds **7**/**10**. The strain of a 6.5.5 product, together with the lower nucleophilicity of the *o*-amino group in structures **6**/**8** may possibly have been the reason for this.

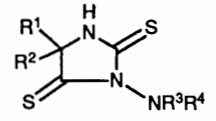
In addition, from thiosemicarbazide, only the imidazolidine-



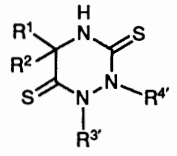
Scheme 1. *Reagents:* R^3I, NEt_3; ii, R^2NH_2.



Scheme 2.



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
(11) **a**;	Ph	Me	H	H	**g**;	Ph	Et	H	H
b;	Ph	Ph	H	H	h;	Ph	Et	Me	H
c;	*p*-Tolyl	Me	H	H	i;	*p*-Tolyl	Me	Me	H
d;	2-naphthyl	Me	H	H	j;	*p*-Tolyl	Me	Me	Me
e;	Ph	Me	Me	H	k;	*p*-Tolyl	Me	Ph	H
f;	Ph	Me	Ph	H	l;	Ph	Ph	Me	H



(12)

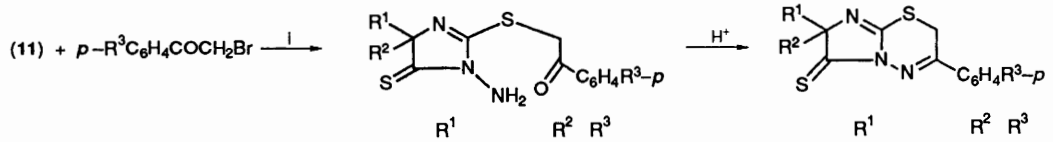
dithione derivative **9** could be obtained, even under drastic reaction conditions. The cyclisation of compound **9** may not have occurred due to ring strain in the 5.5 product and the low nucleophilicity of the thioamide NH_2 group. This is in striking contrast to the reaction of 1,3-thiazine-2,6-dithiones with thiosemicarbazide to give fused heterocycles, [1,2,4]triazolo[1,5-*a*]pyrimidine-2,7-dithiones, in moderate yields.[1]

Hydrazines were particularly reactive toward thiazolidinedithiones to form 1-amino-, -alkylamino- and -anilino-imidazolidine-2,4-dithiones **11** in quantitative yield. The possibility of 1,2,4-triazine-3,6-dithiones **12** instead of compounds **11** being formed was ruled out since imidazo[2,1-*b*][1,3,4]thiadiazine derivatives **14** were produced on treatment of compounds **11a–d** with α-bromoacetophenones. The intermediate compounds **13** were isolated under alkaline reaction conditions and were converted into compounds **14** by ring-closure under acidic conditions (Scheme 3). Molina *et al.*[3] found 1-amino-2-thioxo-1,2-dihydropyridines to react with α-bromocarbonyl compounds to give 1,3,4-thiadiazino[3,2-*a*]pyridinium salts by a reaction similar to that for the formation of compounds **14**.

Compounds **3h** and **3i**, simpler imidazolidines with no substituent on N-3 of the ring, were produced in rather low yield by reactions of thiazolidinedithiones with thiourea in the presence of a strong base in a polar aprotic solvent. Methylthiourea in this reaction merely afforded compound **3h** in very low yield (2%) and it thus follows that thiourea itself does not react directly with the thiazolidinedithiones but with ammonia generated by the decomposition of thiourea under basic reaction conditions to give compounds **3h,i**. Aq. ammonia also reacted with 4-methyl-4-phenylthiazolidinedithione so that compound **3h** was obtained in 56% yield.

Enamino nitriles, different from the above amino-containing nucleophiles, reacted as carbanions to give pyrrole-3(2*H*)-thiones **16**. In this case, a strong base such as t-alkoxide was required to promote the reaction (Scheme 4).

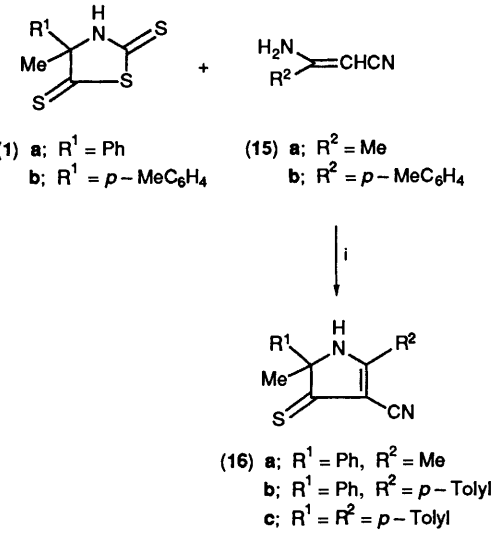
The most active positions for nucleophiles for the reactions with thiazolidinedithiones and with 1,3-thiazine-2,6-dithiones were different; the nucleophiles attack the thiocarbonyl carbon at the 5-position in thiazolidine-2,5-dithiones, while 1,3-thiazine-2,6-dithiones react with the same nucleophiles at the



	R^1	R^2	R^3
(13) **a**;	Ph	Me	H
b;	Ph	Ph	H
c;	Ph	Ph	Br
d;	*p*-Tolyl	Me	H
e;	*p*-Tolyl	Me	Br
f;	2-naphthyl	Me	H
g;	2-naphthyl	Me	Br

	R^1	R^2	R^3
(14) **a**;	Ph	Me	H
b;	Ph	Ph	H
c;	*p*-Tolyl	Me	H
d;	2-naphthyl	Me	H
e;	2-naphthyl	Me	Br

Scheme 3. *Reagent and conditions:* i, NEt_3, room temp.



Scheme 4. *Reagent and conditions:* i, Bu'OK, reflux.

2-position. Abnormal methylation of 4-phenylthiazolidine-2,5-dithione was noted in the previous study but results of calculations for the heat of formation and the contribution of the HOMO to two tautomers, the enethiolic and dithione form of this thiazolidinethione, showed that this methylation was in fact reasonable.[2]

The present data show the thiocarbonyl carbon at the 5-position in thiazolidinedithiones to be exclusive to the reactive site likely to be initially attacked by a nucleophile. The 4-position as well as the thiocarbonyl carbon at the 2-position in thiazinedithiones may be the two most reactive centres in these molecules. However, sterically, the 2-position of thiazinedithiones is much more advantageous than the 4-position for any nucleophile and all reactions gave products corresponding to those whose formation was initiated by the attack of a nucleophile at this position.[1]

Elemental analyses and IR, NMR and some electronic and mass spectra showed good agreement with the proposed structures for compounds **2**–**16** (see Experimental section).

Experimental

M.p.s were measured on a Yanagimoto micro melting point apparatus and are uncorrected. NMR spectra were determined with a JNM-GX270-FT-NMR spectrometer at 270 MHz with tetramethylsilane as internal standard. IR spectra were determined with a JASCO A-302 spectrophotometer. Electronic spectra were obtained on a Hitachi 557 double-wavelength double-beam spectrophotometer.

Starting Materials.—4,4-Disubstituted thiazolidine-2,5-dithiones were prepared by our previous method of synthesis.[2]

4,4-*Disubstituted* 2-*Alkylthiothiazole*-5(4H)-*thiones* **2a**–**c**.—For example, a solution of 4-methyl-4-phenylthiazolidine-2,5-dithione **1a** (10.76 g, 45 mmol), methyl iodide (9.58 g, 67.5 mmol) and triethylamine (5.01 g, 49.5 mmol) in tetrahydrofuran (THF) was kept at room temperature for 1 h. Water (80 ml) was added to the reaction mixture and the resulting mixture was extracted with diethyl ether (100 ml × 3). The combined extract was dried over $MgSO_4$ and evaporated to dryness to give a red oil, which was distilled *in vacuo* to give 4-*methyl*-2-*methylthio*-4-*phenylthiazole*-5(4H)-*thione* **2a** as a red oil (9.88 g, 87%); b.p. 126 °C/0.2 mmHg; m.p. 41.5–42 °C; ν_{max}(KBr) 2960, 2920, 1580, 1563s, 1490, 1442, 1420, 1359, 1303, 1206, 1162, 1100, 1076, 1025, 983s, 951 and 913 cm^{-1}; λ_{max}(EtOH) 280 (log ε 3.72), 317 (3.91), 487 (1.55) and 509 nm (1.47); $\delta_H(CDCl_3)$ 7.3 (5 H, m, Ph), 2.68 (3 H, s, SMe) and 1.94 (3 H, s, Me); $\delta_C(CDCl_3)$ 246.67, 161.92, 140.37, 128.41, 128.01, 125.48, 98.98, 28.72 and 14.74 (Found: C, 52.1; H, 4.2; N, 5.5; S, 37.9. $C_{11}H_{11}NS_3$ requires C, 52.1; H, 4.4; N, 5.5; S, 38.0%).

2-*Ethylthio*-4-*methyl*-4-*phenylthiazole*-5(4H)-*thione* **2b**. Yield 75%, b.p. 155 °C/0.2 mmHg; ν_{max}(neat) 2960, 2930, 2860, 1580, 1563, 1493, 1442, 1370, 1360, 1264, 1169, 1100, 1071, 1028, 959s and 920 cm^{-1}; λ_{max}(EtOH) 278 (3.80), 316 (4.00), 487 (1.55) and 509 nm (1.47); $\delta_H(CDCl_3)$ 7.3 (5 H, m, Ph), 3.28 (2 H, q, *J* 7.3 Hz, SCH_2), 1.91 (3 H, s, Me) and 1.47 (3 H, t, *J* 7.3 Hz, CH_2Me) (Found: C, 53.9; H, 4.8; N, 5.2; S, 35.8. $C_{12}H_{13}NS_3$ requires C, 53.9; H, 4.9; N, 5.2; S, 36.0%).

4-*Methyl*-2-*methylthio*-4-(p-*tolyl*)*thiazole*-5(4H)-*thione* **2c**. Yield 85%, b.p. 136–137 °C/0.065 mmHg; ν_{max}(neat) 2975, 2920, 1563s, 1506, 1441, 1407, 1358, 1309, 1186, 1167, 1100s, 1058, 1019, 983s, 953s and 916 cm^{-1}; λ_{max}(EtOH) 278 (3.77), 317.5 (3.94), 478 (1.76) and 510 nm (1.76); $\delta_H(CDCl_3)$ 7.25 and 7.12 (each 2 H, each d, *J* each 8.3 Hz, C_6H_4), 2.68 (3 H, s, SMe), 2.31 (3 H, s, C_6H_4Me), 1.93 (3 H, s, Me) (Found: C, 53.8; H, 4.8; N, 5.3; S, 35.9. $C_{12}H_{13}NS_3$ requires C, 53.9; H, 4.9; N, 5.2; S, 36.0%).

Preparation of 5,5-*Disubstituted Imidazolidine*-2,4-*dithiones* **3a**–**i**.—*Method A: From the thiazolidinedithiones and Amines. General procedure.* To a suspension of a thiazolidine-2,5-dithione (2 mmol) in 50% ethanol (7 ml) was added an amine (5 mmol). The mixture was warmed to 70 °C to obtain a clear solution, which was kept at room temperature* and then filtered to remove a small quantity of insoluble matter. The filtrate was treated under reduced pressure to remove EtOH, and the yellow crystals which were separated were collected, and washed with water. Yields, m.p.s, solvent for recrystallization and IR spectra of compounds **3a**–**i** are shown in Table 1. NMR data are given in footnotes to Table 1.

Method B. A mixture of 4-methyl-2-methylthio-4-phenylthiazole-5(4H)-thione **2a** (0.506 g, 2 mmol), an amine (5 mmol) and ethanol (7 ml) was warmed to 70 °C for a short time to obtain a clear solution and then the solution was kept at room temperature for 1–2 h. Water (7 ml) was added to the reaction mixture, and EtOH in the aq. solution was removed under reduced pressure; yellow crystals of a compound **3** separated out. The crystals were collected, washed with water and dried. A small amount of compound **3** was also obtained from the acidified filtrate (pH 1). Reaction time and yields by method **B** are listed in Table 1.

5-*Methyl*-5-*phenylimidazolidine*-2,4-*dithione* **3h**. A mixture of 4-methyl-4-phenylthiazolidine-2,5-dithione **1a** (0.24 g, 1 mmol) 1.5M-ammonia water (1.7 ml, 2.5 mmol) and 50% EtOH (5 ml) was warmed at 70 °C for a very short time. The mixture turned into a clear solution, which was kept for 48 h. The reaction mixture was filtered, and EtOH in the filtrate was removed under reduced pressure to give yellow crystals.

5-*Methyl*-5-(p-*tolyl*)*imidazolidine*-2,4-*dithione* **3i**. A solution of methyl-(*p*-tolyl)thiazolidine-2,5-dithione **1b** (1.01 g, 4 mmol), thiourea (0.76 g, 10 mmol) and sodium 1,1-dimethylpropanolate (0.90 g, 4.2 mmol) in *N*,*N*-dimethylformamide (25 ml) was warmed at 85 °C for 1 h. Water (20 ml) was added to the cooled reaction mixture and the resulting aq. solution was washed twice with diethyl ether. The aq. layer, from which any remaining ether was removed under reduced pressure, was acidified with 2M-HCl (pH 1) and was then extracted with diethyl ether. The extract was washed six times with water, dried ($MgSO_4$) and evaporated to dryness to afford a red oil. Yellow

* In this method, the time of storage needed (1–24 h) depended upon the amine employed.

Table 1. 3,5,5-Trisubstituted imidazolidine-2,4-dithiones **3**.

Compd[a]	R^1	R^2	Reaction time (h)	Yield (%)	M.p.[b] (°C)	ν_{max}(KBr) NH	ν_{max}(KBr) hetero ring
3a[c]	Ph	Me	1	99[d]	134.5–135	3150	1520
			1	97[e]	(aq. EtOH)		
3b[f]	Ph	Et	3	91[e]	125.5–126	3160	1513
			1	97[e]	(aq. EtOH)		
3c	Ph	Pr	20	83[d]	72.5–73	3140	1516
			1	99[e]	(C_6H_{14})		
3d[g]	Ph	Pr[i]	1	97[d]	172–172.5	3140	1513
					(aq. EtOH)		
3e	Ph	Bu	24	91[c]	78–78.5	3110	1520
			2	96[e]	(C_6H_{14})		
3f	Ph	c-C_6H_{11}	1	98[e]	185–185.5	3130	1525
					(C_6H_6)		
3g	Ph	Ph	20	45[d]	166.5–168.5	3110	1525
					(EtOH)		
3h[h]	Ph	H	48	56[i]	179.5–180.5	3100	1533
			0.5	36[j]	(C_6H_6–C_6H_{14})		
3i	*p*-Tolyl	H	1	38[j]	213.5–216	3140	1535
					(C_6H_6–C_6H_{14})		

[a] All the compounds gave satisfactory microanalyses. [b] Solvent for recrystallization in parentheses. [c] $\delta_H(CDCl_3)$ 8.89 (1 H, br s, NH), 7.40 (5 H, m, Ph), 3.56 (3 H, s, NMe) and 1.97 (3 H, s, Me); $\delta_C(CDCl_3)$ 207.2, 182.0, 139.1, 128.7, 125.5, 125.0, 75.7, 32.6 and 27.5. [d] Method A. [e] Method B. [f] $\delta_H(CDCl_3)$ 7.3 (5 H, m, Ph), 3.30 (2 H, q, *J* 6.5 Hz, NCH_2), 1.96 (3 H, s, Me) and 1.47 (3 H, t, CH_2Me). [g] $\delta_H(CD_3SOCD_3)$ 11.46 (1 H, br s, NH), 7.35 (5 H, m, Ph), 5.42 (1 H, sept, *J* 6.4 Hz, NCH) and 1.57 and 1.53 (total 6 H, each d, each *J* 6.4 Hz, $CHMe_2$); $\delta_C(CD_3SOCD_3)$ 207.4 (br), 180.8 (br), 139.9, 128.5, 128.1, 125.4, 74.6, 49.2, 26.2 and 17.5 (br). [h] $\delta_H(CD_3COCD_3)$ 11.98 (1 H, br s, NH), 9.88 (1 H, br s, NH), 7.40 (5 H, m, Ph) and 1.93 (3 H, s, Me); $\delta_C(CD_3SOCD_3)$ 210.8, 181.5, 140.5, 129.3, 129.0, 78.4 and 26.9. [i] From the reaction with ammonia. [j] From the reaction with thiourea.

crystals were obtained by treatment of this red oil with hexane and the product was recrystallized from hot benzene–hexane to give yellow crystals of compound **3i**.

1,4-*Dimethyl*-5-*methylimino*-4-*phenylimidazolidine*-2-*thione* **4**.—A solution of 4-methyl-4-phenylthiazolidine-2,5-dithione **1a** (0.48 g, 2 mmol) and aq. methylamine (40%; 4.66 g, 60 mmol) in 50% EtOH (3 ml) was refluxed at 70 °C for 2 h. EtOH was removed from the reaction mixture under reduced pressure, and pale yellow crystals separated out and were collected. The mother liquor was acidified with 2M-HCl (pH 1) to give a second crop of yellow crystals. Both sets of crystals were column chromatographed on silica gel with benzene as eluant to give compound **4** (0.246 g, 53%). Recrystallization from hot benzene–hexane gave pure *compound* **4** as long plates, m.p. 184.5–186 °C; ν_{max}(KBr) 3140s, 2910, 1688s, 1498s, 1441, 1388, 1372, 1320s, 1232, 1183, 1125, 1092, 1043, 1028 and 947 cm^{-1}; λ_{max}(EtOH) 261 nm (4.50); $\delta_H(CDCl_3)$ 7.54 (1 H, br s, NH), 7.3 (5 H, m, Ph), 3.31 (3 H, s, NMe), 2.92 (3 H, s, =NMe) and 1.94 (3 H, s, Me); $\delta_C(CDCl_3)$ 181.1, 160.1, 137.9, 129.2, 128.9, 126.0, 64.4, 35.8 and 29.0; *m*/*z* (70 eV) 233 (M^+, 100%), 218 ($M^+ - CH_3$, 13), 162 [Ph(Me)C=N=C=S$^+$, 15], 145 [Ph(Me)C=C=NMe$^+$, 13] and 119 [Ph(Me)CNH$^+$, 35] (Found: C, 61.9; H, 6.6; N, 17.9; S, 13.9. $C_{12}H_{15}N_3S$ requires C, 61.8; H, 6.5; N, 18.0; S, 13.7%).

3-(2-*Aminoethyl*)-5-*methyl*-5-(p-*tolyl*)*imidazolidine*-2,4-*dithione* **6**.—A solution of 4-methyl-4-(*p*-tolyl)thiazolidine-2,5-dithione **1b** (1.01 g, 4 mmol) and ethylenediamine (0.721 g, 12 mmol) in ethanol (12 ml) was warmed for 3 h at 70 °C. 2M-HCl was added (pH 2) to the cooled reaction mixture to give a small amount of solid, which was collected. The mother liquor was made alkaline (pH 9) with 2M-NaOH under reduced pressure; a pale yellow solid separated out, which was collected and washed with 20% EtOH. Both solids were combined and recrystallized from hot isopropyl alcohol to give the *title compound* **6** as pale yellow crystals (0.9 g, 70%, m.p. 245–245.5 °C; ν_{max}(KBr) 3340, 3260, 3100, 2920, 1550, 1509, 1427, 1345, 1283, 1178, 1143, 1099, 1061 and 1003 cm^{-1}; λ_{max}(EtOH) 228 (4.03) and 304 nm (4.32); *m*/*z* (70 eV) 279 (M^+, 3%), 262 ($M^+ - NH_3$, 15), 237 ($M^+ - CH_2CH{=}NH$, 43), 203 ($M^+ - NH_3 - HNCS$, 40), 176 [C_7H_7(Me)C=NCS$^+$, 21], 162 [C_7H_7(Me)C=C=S$^+$, 24] and 43 ($CH_2{=}CHNH_2$, 100) (Found: C, 56.1; H, 6.0; N, 15.3; S, 23.1. $C_{13}H_{17}N_3S_2$ requires C, 55.9; H, 6.1; N, 15.0; S, 23.0%).

Reaction of o-*Phenylenediamine with* 4,4-*Disubstituted Thiazolidine*-2,5-*dithiones. Formation of* 5,5-*Disubstituted* 3-(2-*Aminophenyl*)*imidazolidine*-2,4-*dithiones* **8a–c**.—A solution of a 4,4-disubstituted thiazolidine-2,5-dithione (4 mmol) and *o*-phenylenediamine (0.864 g, 8 mmol) in EtOH (12 ml) was warmed for 3 h at 70 °C. 2M-HCl(8 ml) was added dropwise to the cooled reaction mixture under reduced pressure. To the acidified mixture was added water (20 ml) and the mixture was kept for 24 h. The solid which separated out was collected and washed with 20% EtOH.

3-(2-*Aminophenyl*)-5-*ethyl*-5-*phenylimidazolidine*-2,4-*dithione* **8a**. Yield 83%, m.p. 271–272 °C (rapid heating), 263–263.5 °C (slow heating) (from hot EtOH–hexane); ν_{max}(KBr) 3450, 3360, 3120, 2960, 1617, 1520s, 1459, 1442, 1381, 1310, 1287s, 1212s and 1192s cm^{-1}; λ_{max}(EtOH) 301 (4.34) and 410 nm (2.00); *m*/*z* (70 eV) 327 (M^+, 58%), 294 ($M^+ - SH$, 100), 235 ($M^+ - C_6H_4NH_2$, 19) and 161 [MeCH=C(Ph)CS$^+$, 53] (Found: C, 62.2; H, 5.4; N, 12.8; S, 19.6. $C_{17}H_{17}N_3S_2$ requires C, 62.4; H, 5.2; N, 12.8; S, 19.6%).

3-(2-*Aminophenyl*)-5-*methyl*-5-(p-*tolyl*)*imidazolidine*-2,4-*dithione* **8b**. Yield 87%, m.p. 183.5–184.5 °C (rapid heating), 180.5–181 °C (slow heating) (from hot EtOH–hexane); ν_{max}(KBr) 3400, 3320, 3200, 2970, 1610, 1500s, 1450, 1381, 1363, 1293s, 1202, 1147, 1130 and 1104 cm^{-1}; λ_{max}(EtOH) 301 (4.35) and 410 nm (2.00); *m*/*z* (70 eV) 327.088 (M^+. *M* requires 327.087, 18%), 294.105 ($M^+ - SH$. *M* – SH requires 294.107, 22), 235.025 ($M^+ - C_6H_4NH_2$. *M* – C_6H_6N requires 235.037, 7) and 161.040 [$CH_2{=}C(C_7H_7)CS^+$. $C_{10}H_9S$ requires 161.043, 16] (Found: C, 62.3; H, 5.4; N, 12.6; S, 19.7. $C_{17}H_{17}N_3S_2$ requires C, 62.4; H, 5.2; N, 12.8; S, 19.6%).

3-(2-*Aminophenyl*)-5-*methyl*-5-(2-*naphthyl*)*imidazolidine*-2,4-*dithione* **8c**. Yield 93%, m.p. 232.5–233 °C (from hot EtOH–hexane); ν_{max}(KBr) 3430, 3360, 3100, 2970, 1617, 1520s, 1502s, 1459, 1377, 1350, 1290s, 1228s, 1208, 1188, 1150, 1131 and 1118 cm^{-1}; λ_{max}(EtOH) 294 (4.39) and 410 nm (2.21); *m/z* (70 eV) 363 (M^+, 52%), 330 (M^+ − SH, 100), 304 (M^+ − HNCS, 10), 271 (M^+ − $C_6H_4NH_2$, 35) and 197 [CH_2=C($C_{10}H_7$)CS^+, 16] (Found: C, 65.9; H, 4.6; N, 11.5; S, 17.6. $C_{20}H_{17}N_3S_2$ requires C, 66.1; H, 4.7; N, 11.6; S, 17.6%).

Compounds **8a–c** were never converted into corresponding benzimidazolethiones on refluxing for 5 h in EtOH.

5-*Methyl*-3-*thioureido*-5-(p-*tolyl*)*imidazolidine*-2,4-*dithione* **9**.—To a mixture of 4-methyl-4-(*p*-tolyl)thiazolidine-2,5-dithione **1b** (0.253 g, 1 mmol), potassium hydroxide (0.112 g, 2 mmol) and EtOH (7 ml) was added a solution of thiosemicarbazide hydrochloride (0.256 g, 2 mmol) in water (4 ml). The mixture was warmed for 3 h at 70 °C and then cooled. The reaction mixture was filtered and the filtrate was diluted with water (10 ml) and acidified with 2M-HCl (pH 1) to give a yellow solid, which was collected, washed with water and recrystallized from xylenes–ethanol–hexane to give *compound* **9** as yellow crystals (0.184 g, 59%), m.p. 213–314 °C (rapid heating), 207.5–208 °C (slow heating); ν_{max}(KBr) 3300, 3240, 3130, 1608, 1508, 1440, 1402, 1350, 1300, 1211, 1102, 1060 and 1013 cm^{-1} (Found: C, 46.6; H, 4.5; N, 17.8. $C_{12}H_{13}N_3S_2$ requires C, 46.3; H, 4.55; N, 18.05%).

2,3,6,7-*Tetrahydro*-7-*methyl*-7-(p-*tolyl*)-5H-*imidazo*[5,1-*a*]-*imidazole*-5-*thione* **7a**.—A solution of 4-methyl-4-(*p*-tolyl)-thiazolidine-2,5-dithione (2.02 g, 8 mmol) and ethylenediamine (1.44 g, 24 mmol) in EtOH (25 ml) was warmed for 24 h at 70 °C. The hot reaction mixture was filtered and then cooled to room temperature to give lustrous crystals on prolonged storage, which were collected and washed three times with carbon disulphide. Recrystallization from hot ethanol gave the *title compound* **7a** as crystals (0.70 g, 71%), m.p. 247 °C; ν_{max}(KBr) 3190, 2930, 2760, 1677s, 1503s, 1425, 1350s, 1276, 1224, 1180, 1142, 1105, 1082, 1070, 1019, 983 and 964 cm^{-1}; λ_{max}(EtOH) 263 nm (4.26); δ_H(C_5D_5N) 8.71 (1 H, br s, NH), 7.3 (4 H, m, C_6H_4), 4.60 (2 H, t, *J* 6.8 Hz, =NCH_2), 3.28 (2 H, t, *J* 6.8 Hz, NCH_2), 2.18 (3 H, s, C_6H_4*Me*) and 2.02 (3 H, s, Me) (Found: C, 63.6; H, 6.3; N, 17.0. $C_{13}H_{15}N_3S$ requires C, 63.7; H, 6.2; N, 17.1%).

3,4,7,8-*Tetrahydro*-8-*methyl*-8-(p-*tolyl*)-2H,6H-*imidazo*[5,1-a]*pyrimidine*-6-*thione* **7b**.—A solution of 4-methyl-4-(*p*-tolyl)-thiazolidine-2,5-dithione **1b** (1.01 g, 4 mmol) and trimethylenediamine (0.89 g, 12 mmol) in EtOH (13 ml) was warmed for 3 h at 70 °C and then cooled to −12 °C. The resulting white solid was collected, washed with a mixed solvent of EtOH and hexane (4:6), and recrystallized from hot ethanol to give *compound* **7b** as crystals (0.78 g, 75%), m.p. 235 °C; ν_{max}(KBr) 3110, 2950, 2930, 1670s, 1492s, 1438, 1409, 1359, 1340, 1328, 1300s, 1260, 1238, 1200, 1107, 1038, 1020 and 952 cm^{-1}; λ_{max}(EtOH) 261 nm (4.42); δ_H($CDCl_3$) 7.61 (1 H, br s, NH), 7.32 and 7.18 (each 2 H, each d, *J* 8 Hz, C_6H_4), 3.82 (2 H, t, *J* 6.8 Hz, =NCH_2), 3.44 (2 H, t, *J* 6.8 Hz, NCH_2), 2.33 (3 H, s, C_6H_4*Me*), 1.94 (2 H, m, $CH_2CH_2CH_2$) and 1.82 (3 H, s, Me); δ_C(C_5D_5N) 179.6, 158.0, 138.6, 136.8, 128.8, 125.2, 64.2, 43.8, 26.3, 20.5 and 19.3; *m/z* (70 eV) 259 (M^+, 100%) and 244 (M^+ − CH_3, 3) (Found: C, 64.8; H, 6.6; N, 16.1; S, 12.6. $C_{14}H_{17}N_3S$ requires C, 64.8; H, 6.6; N, 16.2; S, 12.35%).

8,9-*Dihydro*-8-*methyl*-8-(p-*tolyl*)*imidazo*[1,5-a]*perimidine*-10-*thione* **10**.—A solution of 4-methyl-4-(*p*-tolyl)thiazolidine-2,5-dithione **1b** (1.01 g, 4 mmol) and naphthalene-1,8-diamine (1.90 g, 12 mmol) in EtOH (12 ml) was warmed for 3 h at 70 °C and then cooled. The reaction mixture was acidified with 2M-HCl pH 2) followed by the addition of water (5 ml) to give yellow crystals. Recrystallization from hot isopropyl alcohol gave *compound* **10** as yellow crystals (1.34 g, 97%), m.p. 215.5–216 °C; ν_{max}(KBr) 3380, 1664s, 1595, 1590, 1512, 1473s, 1402s, 1372, 1339, 1258s, 1228, 1210, 1175, 1162, 1108 and 1077 cm^{-1}; λ_{max}(EtOH) 225 (4.48, 233 (4.47), 291 (4.08), 334 (4.06), 348 (4.03), 380 (3.83), 398 (3.83) and 420 nm (3.50) (Found: C, 73.1; H, 5.3; N, 11.9; S, 9.6. $C_{21}H_{17}N_3S$ requires C, 73.4; H, 5.0; N, 12.2; S, 9.3%).

Preparation of 5,5-*Disubstituted* 3-*Amino- and -Alkylamino-imidazolidine*-2,4-*dithiones* **11a–l**.—*General procedure*. To a stirred solution of a 4,4-disubstituted thiazolidine-2,5-dithione (2 mmol) in EtOH (12 ml) was added dropwise a hydrazine $NH_2NR^3R^4$ (4 mmol). The mixture was kept for 3 h at room temperature. Water (15 ml) was added to the reaction mixture and this aq. solution was acidified with 2M-HCl (pH 1); an oil separated out, and solidified within a few min. The solid was collected, washed with water, dried and recrystallized. Yields, m.p.s and ν_{max}(KBr) values are given in Table 2.

Reaction of Compounds **11** *with* 4′-*Substituted* α-*Bromoacetophenones. Isolation of Intermediates*, 5,5-*Disubstituted* 3-*Amino*-2-(*benzoylmethylthio*)*imidazole*-4(5H)-*thiones* **13**.—*General procedure*. A mixture of a compound **11** (2 mmol), phenacyl bromide or 4′-bromophenacyl bromide (2 mmol), triethylamine (4 mmol) and dry benzene (17 ml) was refluxed for 2.5 h. Triethylammonium bromide which separated out and filtered off, and the filtrate was condensed to give yellow crystals, which were collected, washed with hexane and recrystallized from hot EtOH–water to give yellow crystals of compounds **13**. Yields, m.p.s and ν_{max}(KBr) are shown in Table 3.

Imidazo[2,1-b][1,3,4]*thiadiazines* **14**. For example, conc. sulphuric acid (0.055 g, 1 mmol) was added to a solution of compound **11a** (0.355 g, 1 mmol) in EtOH (5 ml) and the solution was warmed for 1 h at 78 °C and cooled. Water (10 ml) was added to the solution and the aq. solution was then extracted with diethyl ether (20 ml × 2). The combined extract was dried over $MgSO_4$ and evaporated to give an oil, which was dissolved in benzene (5 ml). Addition of hexane to this solution caused a crystalline solid to separate out (0.304 g, 90%), which was recrystallized from hot EtOH–water to give yellow crystals of 7-methyl-3,7-diphenyl-2*H*,7*H*-imidazo[2,1-*b*][1,3,4]thiadiazine-6-thione **14a**. Compounds **14b–e** were also obtained by a similar reaction. Yields, m.p.s, solvent for recrystallization and spectral data of compounds **14a–e** are shown in Table 3.

Direct Synthesis of Compounds **14** *from Compounds* **11**. For example, a solution of compound **6a** (0.475 g, 2 mmol) and phenacyl bromide (0.398 g, 2 mmol) in benzene (20 ml) was refluxed for 2 h. Hydrobromide of compound **14a** separated from the solution. Triethylamine (0.405 g, 4 mmol) was added to the reaction mixture without filtration and then the resulting mixture was stirred for 0.5 h. The reaction mixture was filtered to remove triethylammonium bromide to obtain benzene solution, which was concentrated and followed by the addition of hexane. Yellow solid which separated was collected, washed with hexane and recrystallized from hot EtOH–water to give pure compound **14a**. IR spectrum and m.p. were identical with those of the compound obtained by conversion of compound **13a**.

Reaction with Enamino Nitriles. Formation of Pyrrole-3(2H)-*thiones* **16**.—*General procedure*. A mixture of a 4-aryl-4-methylthiazolidine-2,5-dithione (2 mmol), an enamino nitrile (2.5 mmol), potassium t-butoxide (0.696 g, 5.7 mmol) in THF (30 ml) was refluxed for 23 h and then water (30 ml) was added to the cooled reaction mixture. The aq. solution was washed

Table 2. 3-Aminoimidazolidine-2,4-dithiones **11**.

Compd[a]	R^1	R^2	R^3	R^4	Yield (%)	M.p.[b] (°C)	ν_{max}(KBr) NH_2	ν_{max}(KBr) hetero ring
11a[c]	Ph	Me	H	H	67	145–146.5 (C_6H_6–C_6H_{14})	3260, 3140	1510
11b[d]	Ph	Ph	H	H	93	220.5–222 (aq. EtOH)	3270, 3160	1508
11c[e]	*p*-Tolyl	Me	H	H	92	137–138 (C_6H_6–C_6H_{14})	3280, 3140	1518
11d	2-Naphthyl	Me	H	H	94	154–155 (aq. THF)	3370, 3150	1510
11e	Ph	Me	Me	H	81	128.5–129 (C_6H_6–C_6H_{14})	3200	1510
11f	Ph	Me	Ph	H	99	175.5–176 (aq. EtOH)	3210	1518
11g[f]	Ph	Et	H	H	94	118.5–119 (aq. EtOH)	3350, 3155	1515
11h	Ph	Et	Me	H	99	129.5–130 (EtOH–C_6H_{14})	3160	1522
11i	*p*-Tolyl	Me	Me	H	94	141.5–142.5 (aq. EtOH)	3200	1512
11j[g]	*p*-Tolyl	Me	Me	Me	92	182–184 (C_6H_6–C_6H_{14})	3140	1492
11k	*p*-Tolyl	Me	Ph	H	98	213.5–214.5 (C_6H_6–C_6H_{14})	3360, 3240	1510
11l	Ph	Ph	Me	H	81	164.5–165.5 (aq. EtOH)	3160	1510

[a] All the compounds gave satisfactory micronalyses. [b] Solvent for recrystallization in parentheses. [c] $\delta_H(CD_3COCD_3)$ 10.29 (1 H, br s, NH), 7.4 (5 H, m, Ph), 5.99 (2 H, br s, NH_2) and 1.94 (3 H, s, Me). [d] $\delta_H(CD_3COCD_3)$ 10.24 (1 H, br s, NH), 7.4 (5 H, m, Ph), 6.02 (2 H, br s, NH_2), 2.48 and 2.37 (each 1 H, each d, q, each *J* 13 and 7 Hz, CH_2Me) and 0.84 (3 H, t, *J* 7 Hz, CH_2Me). [e] $\delta_H(CD_3COCD_3)$ 10.68 (1 H, br s, NH), 7.40 (10 H, m, *Ph* × 2) and 6.13 (2 H, br s, NH_2). [f] $\delta_H(CD_3SOCD_3)$ 11.57 (1 H, br s, NH), 7.20 (4 H, s, C_6H_4), 6.02 (2 H, br s, NH_2), 2.28 (3 H, s, C_6H_4Me) and 1.78 (3 H, s, Me); $\delta_C(CD_3SOCD_3)$ 197.3, 177.5, 137.6, 136.3, 129.0, 125.4, 73.4, 26.0 and 20.4. [g] $\delta_H(CD_3COCD_3)$ 10.26 (1 H, br s, NH), 8.07 (2 H, br s, NH_2), 7.0 (9 H, s, C_6H_4 + *Ph*NH), 2.32 (3 H, s, C_6H_4Me) and 2.01 (3 H, s, Me).

Table 3. 5,5-Disubstituted 3-amino-2-(benzoylmethylthio)-3,5-dihydro-4*H*-imidazole-4-thiones **13** and imidazo[2,1-*b*][1,3,4]thiadiazines **14**.

Compd[a]	R^1	R^2	R^3	Yield (%)	M.p.[b] (°C)	ν_{max}(KBr) NH_2	C=O	C=N
13a	Ph	Me	H	100	156.6–157.5 (aq. EtOH)	3310, 3251	1683	1610
13b[c]	Ph	Ph	H	88	151.5–152 (aq. EtOH)	3280, 3250	1677	1587
13c	Ph	Ph	Br	97	168.5–169.5 (CH_2Cl_2–C_6H_{12})	3300, 3200	1680	1623
13d	*p*-Tolyl	Me	H	99	153–154 (CH_2Cl_2–C_6H_{12})	3315, 3250	1685	1610
13e	*p*-Tolyl	Me	Br	100	164.5–165.5 (CH_2Cl_2–C_6H_{12})	3300, 3200	1682	1583
13f	2-Naphthyl	Me	H	93	160.5–161.5 (aq. EtOH)	3300, 3180	1685	1618
13g	2-Naphthyl	Me	Br	100	132–134 (aq. EtOH)	3300, 3200	1688	1588
14a	Ph	Me	H	94	149 (aq. EtOH)			1600
14b[d]	Ph	Ph	H	93	180.5–181.5 (aq. EtOH)			1599
14c	*p*-Tolyl	Me	H	96	160–160.5 (CH_2Cl_2–C_6H_{12})			1591
14d	2-Naphthyl	Me	H	100	213–215 (C_6H_6)			1595
14e	2-Naphthyl	Me	Br	49	132–134 (EtOH–C_6H_{12})			1595

[a] All the compounds gave satisfactory microanalyses. [b] Solvent for recrystallization in parentheses. [c] $\delta_H(CD_3COCD_3)$ 7.5 (15 H, m, Ph × 3), 5.46 (2 H, s, NH_2) and 4.92 (2 H, s, CH_2). [d] $\delta_H(CD_3COCD_3)$ 7.5 (15 H, m, Ph × 3) and 4.46 (2 H, s, CH_2).

with diethyl ether and treated under reduced pressure to remove any remaining ether. Acidification (pH 4) with 2M-HCl gave a yellow solid, which was collected, washed with water, dried and recrystallized to give the corresponding pyrrole-3-(2*H*)-thione **16**.

4-*Cyano*-2,5-*dimethyl*-2-*phenylpyrrole*-3(2H)-*thione* **16a**.* Yield 68%, m.p. 203 °C (from acetone–water); ν_{max}(KBr) 3220, 2210, 1600, 1550, 1500, 1480, 1450, 1432, 1370, 1354, 1317, 1260, 1159, 1082 and 1030 cm^{-1}; λ_{max}(EtOH) 264 (3.90) and 370 nm (4.31); $\delta_H(CD_3COCD_3)$ 10.30 (1 H, br s, NH), 7.34 (5 H, m, Ph), 2.59 (3 H, s, 5-Me) and 1.81 (3 H, s, 2-Me); $\delta_C(CD_3COCD_3)$ 223.7, 178.0, 177.9, 139.6, 129.2, 128.8, 126.5, 115.9, 103.0, 81.7, 26.9 and 15.1 (Found: C, 68.4; H, 5.4; N, 12.0; S, 14.0. $C_{13}H_{12}N_2S$ requires C, 68.4; H, 5.3; N, 12.3; S, 14.0%).

4-*Cyano*-2-*methyl*-2-*phenyl*-5-(p-*tolyl*)*pyrrole*-3(2H)-*thione* **16b**.† Yield 38%; m.p. 280–281 °C (from acetone–water); ν_{max}(KBr) 3200, 2220, 1610, 1555, 1502, 1465, 1432, 1370, 1354, 1317, 1305, 1255, 1212, 1186, 1155, 1076, 1055 and 1026 cm^{-1}; λ_{max}(EtOH) 276 (4.44) and 398 nm (4.28); $\delta_H(CD_3SOCD_3)$ 11.70 (1 H, br s, NH), 8.00 and 7.54 (each 2 H, each d, *J* 8.5 Hz, C_6H_4), 7.35 (5 H, ~s, Ph), 2.46 (3 H, s, C_6H_4Me), 1.84 (3 H, s, 2-Me); $\delta_C(CD_3SOCD_3)$ 223.1, 172.0, 144.7, 138.7, 129.9, 128.5, 125.6, 123.7, 116.6, 98.5, 80.2, 26.2 and 21.2 (Found: C, 74.9; H, 5.4; N, 8.8; S, 10.8. $C_{19}H_{16}N_2S$ requires C, 75.0; H, 5.3; N, 9.2; S, 10.5%).

4-*Cyano*-2-*methyl*-2,5-*di*-(p-*tolyl*)*pyrrole*-3(2H)-*thione* **16c**.‡ Yield 58%; m.p. 236–239 °C (from acetone–water); ν_{max}(KBr) 3200, 2220, 1610, 1550, 1500, 1467, 1328, 1320, 1306, 1280, 1252, 1187, 1157, 1104, 1073 and 1012 cm^{-1}; $\delta_C(CD_3SOCD_3)$ 11.65 (1 H, br s, NH), 8.00 and 7.54 (each 2 H, each d, *J* 8.5 Hz, 5-C_6H_4), 7.21 and 7.17 (each 2 H, each d, *J* 8 Hz, 2-C_6H_4), 2.45 (3 H, s, 5-C_6H_4Me), 2.28 (3 H, s, 2-C_6H_4Me), 1.84 (3 H, s, 2-Me); $\delta_C(CD_3SOCD_3)$ 223.3, 171.8, 144.7, 137.3, 135.9, 129.9, 129.0, 128.4, 125.5, 123.7, 116.7, 98.4, 80.0, 26.2, 21.2 and 20.5 (Found: C, 75.2; H, 5.65; N, 8.5; S, 10.1. $C_{20}H_{18}N_2S$ requires C, 75.4; H, 5.7; N, 8.8; S, 10.1%).

* *Systematic name:* 4,5-dihydro-2,5-dimethyl-5-phenyl-4-thioxopyrrole-3-carbonitrile.

† *Systematic name:* 4,5-dihydro-5-methyl-5-phenyl-2-(*p*-tolyl)pyrrole-3-carbonitrile.

‡ *Systematic name:* 4,5-dihydro-5-methyl-2,5-di-(*p*-tolyl)pyrrole-3-carbonitrile.

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