The Synthesis and Properties of some Novel 5-Amino-1,4,2-dithiazolium Salts and the *X*-Ray Molecular structure of 5-Morpholino-3-(4-nitrophenyl)-1,4,2-dithiazolium Fluoroborate

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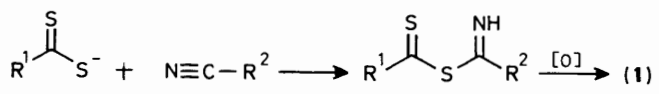
Reaction of dithiocarbamate salts, either with α-bromo iminium salts followed by oxidative bromination, or simply with α-chloro oxime *O*-sulphonates, leads to novel 5-amino-1,4,2-dithiazolium salts. Reaction of the salts with sodium borohydride, or with active methylene compounds in the presence of base, gives products analogous to those from 1,3-dithiolium salts, although the former reduction products fail to eliminate the 5-amino group on treatment with acid. The crystal structure of 5-morpholino-3-(4-nitrophenyl)-1,4,2-dithiazolium fluoroborate is reported. This, and n.m.r. evidence, indicates that most of the positive charge resides on the exocyclic nitrogen atom.

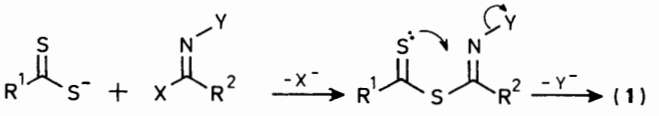
Although the 1,4,2-dithiazolium cation (**1**) might be expected to have a chemistry as diverse and interesting as that of the analogous 1,3-dithiolium cation (**2**),[1] it remained unknown until 1985 in the absence, apparently, of serious attempts to prepare it. Three different synthetic approaches to the cation have now been published,[2–4] illustrating the growing interest in this species. We report here more fully on one of these approaches.[3]

(**1**) (**2**)

Our objective was to develop a general synthesis of the cation (**1**) which allowed the greatest possible variation of the substituents R^1 and R^2. This objective was potentially achievable using the strategies shown in Schemes 1 and 2. Both approaches were attempted.



Scheme 1.

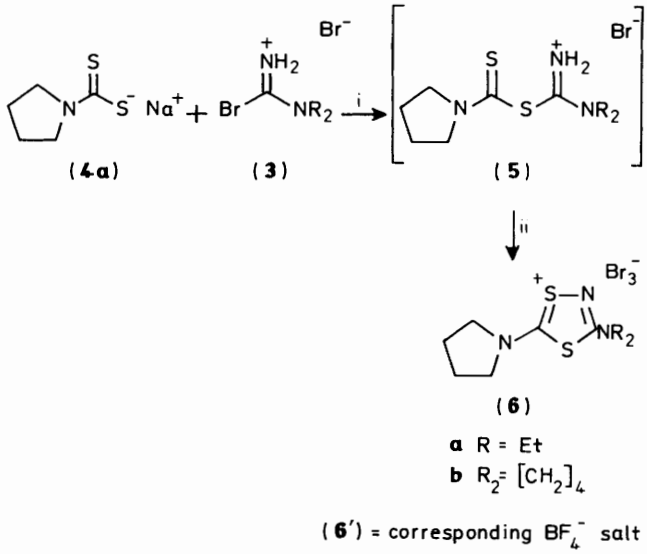


Scheme 2.

Results and Discussion

Dithiocarbamate salts were used throughout this work to provide the ring atoms 1, 4, and 5. This choice resulted from their stability, ready accessibility, and greater nucleophilicity as compared with dithiocarboxylate salts.

Preparations from Nitrile Derivatives with Oxidation.—While dithiocarboxylates have been reported to add to imines,[5] successful addition of dithiocarbamates to the less electrophilic nitrile group required preliminary activation of the latter. Dry hydrogen chloride is known to add to cyanamides to give relatively stable chloroformamidinium chlorides.[6] We chose to use the analogous bromo compounds in view of the potentially greater lability of the bromine atom. Addition of dry hydrogen bromide to a solution of diethylcyanamide in anhydrous ether gave the salt (**3a**) (65%) as a pale yellow hygroscopic powder, with i.r. and ^{1}H n.m.r. spectra consistent with the proposed structure. This salt was added to a solution of the anhydrous dithiocarbamate (**4a**)† in dry methanol at 5 °C, and the resulting solution, after being stirred for 1 h, was treated with bromine to oxidise the presumed intermediate (**5a**) (Scheme 3). Orange plates separated, which proved to be the 1,4,2-dithiazolium tribromide (**6a**) in low yield. The structure was confirmed from the mass spectrum, which showed the parent ion at *m/z* 244.0939 ($C_{10}H_{18}N_3S_2$ requires *M*, 244.0942) as well as prominent fragments corresponding to $C_4H_8N{-}C{\equiv}S^+$ and $Et_2N{-}C{\equiv}N^{+\bullet}$, and from analytical and other spectroscopic data (Tables 2 and 3). Treatment with cyclohexene, followed by sodium fluoroborate, gave the



(**4a**) (**3**) (**5**) (**6**)

a R = Et
b R_2 = $[CH_2]_4$

(**6'**) = corresponding BF_4^- salt

Scheme 3. *Reagents and condition:* i, MeOH, 5 °C; ii, Br_2

† Prepared *in situ* by dissolving sodium in absolute methanol and adding CS_2 and pyrrolidine.

Table 1. I.r. and ^{1}H n.m.r. spectroscopic data for the intermediates (**11**)—(**14**)

Compound	$\nu_{max.}$(Nujol)/cm^{-1}	δ_H($CDCl_3$)
(**11a**)	1 590, 1 540, 1 460, 1 425, 1 360, 1 165, 988, 841, and 790	2.15 (4 H, m), 3.25 (3 H, s), 3.82 (4 H, m), 7.4—7.6 (3 H, m), and 7.8—8.0 (2 H, m)
(**11c**)		3.28 (3 H, s), 3.80 (4 H, m), 4.14 (4 H, m), 7.5—7.7 (3 H, m), and 7.9—8.1 (2 H, m)
(**12a**)	1 587, 1 439, 1 365, 1 179, 955, 835, and 810	2.08 (4 H, m), 3.25 (3 H, s), 3.80 (4 H, m), 7.37 (2 H, m), and 7.82 (2 H, m)
(**12b**)	1 595, 1 438, 1 372, 1 187, 965, 872, and 815	1.77 (6 H, m), 3.22 (3 H, s), 4.08 (4 H, m), 7.42 (2 H, m), and 7.84 (2 H, m)
(**12c**)	1 593, 1 435, 1 370, 1 233, 1 188, 1 112, 964, 884, and 813	3.27 (3 H, s), 3.80 (4 H, m), 4.17 (4 H, m), 7.44 (2 H, m), and 7.85 (2 H, m)
(**12d**)	1 588, 1 385, 1 371, 1 191, 1 175, 966, 865, and 807	3.24 (3 H, s), 3.44 (3 H, s), 3.51 (3 H, s), 7.39 (2 H, m), and 7.81 (2 H, m)
(**12e**)		1.25 (3 H, t), 1.40 (3 H, t), 3.23 (3 H, s), 3.90 (4 H, q), 7.38 (2 H, m), and 7.82 (2 H, m)
(**13a**)	1 595, 1 530, 1 382, 1 360, 1 189, 979, 925, 866, and 816	2.08 (4 H, m), 3.32 (3 H, s), 3.83 (4 H, m), 7.63 (1 H, t), 8.2—8.5 (2 H, m), and 8.68 (1 H, t)
(**13b**)	1 588, 1 537, 1 376, 1 365, 1 355, 1 187, 972, 857, and 815	1.78 (6 H, m), 3.29 (3 H, s), 4.08 (4 H, m), 7.62 (1 H, t), 8.2—8.5 (2 H, m), and 8.69 (1 H, t)
(**13c**)	1 586, 1 530, 1 372, 1 358, 1 346, 1 192, 985, 856, and 808	3.30 (3 H, s), 3.83 (4 H, m), 4.17 (4 H, m), 7.65 (1 H, t), 8.2—8.5 (2 H, m), and 8.70 (1 H, t)
(**13d**)	1 584, 1 535, 1 373, 1 360, 1 191, 977, 853, and 813	3.29 (3 H, s), 3.45 (3 H, s), 3.56 (3 H, s), 7.63 (1 H, t), 8.2—8.4 (2 H, m), and 8.70 (1 H, t)
(**13e**)	1 585, 1 538, 1 380, 1 367, 1 193, 976, 858, and 814	1.24 (3 H, t), 1.45 (3 H, t), 3.29 (3 H, s), 3.91 (4 H, q), 7.64 (1 H, t), 8.2—8.4 (2 H, m), and 8.68 (1 H, t)
(**14a**)	1 594, 1 522, 1 371, 1 347, 1 186, 972, 851, and 812	2.12 (4 H, m), 3.30 (3 H, s), 3.83 (4 H, m), 8.09 (2 H, m), and 8.27 (2 H, m)
(**14b**)	1 605, 1 595, 1 523, 1 380, 1 350, 1 191, 965, 853, and 813	1.77 (6 H, m), 3.30 (3 H, s), 4.23 (4 H, m), 8.09 (2 H, m), and 8.28 (2 H, m)
(**14c**)	1 608, 1 599, 1 521, 1 383, 1 347, 1 191, 1 033, 969, 853, and 813	3.28 (3 H, s), 3.80 (4 H, m), 4.17 (4 H, m), 8.06 (2 H, m), and 8.26 (2 H, m)
(**14d**)	1 605, 1 524, 1 371, 1 351, 1 193, 981, 853, and 812	3.27 (3 H, s), 3.45 (3 H, s), 3.55 (3 H, s), 8.08 (2 H, m), and 8.27 (2 H, m)
(**14e**)	1 605, 1 524, 1 378, 1 350, 1 192, 967, 852, and 810	1.26 (3 H, t), 1.45 (3 H, t), 3.30 (3 H, s), 3.95 (4 H, q), 8.08 (2 H, m), and 8.28 (2 H, m)

Table 2. Physical, analytical, and i.r. spectroscopic data for 1,4,2-dithiazolium salts (**6**) and (**15**)—(**18**)

Compound (Formula)	Yield (%)	M.p. (°C)	Solvent	Found (%) (Requires) C	H	N	$M^{+\cdot}$	$\nu_{max.}$ (Nujol/cm^{-1}
(**6a**)	15	141—144	MeOH	24.65	3.3	8.4	244	1 596, 1 550, 1 435, 1 332, 1 200, 980, 750, and 610
($C_{10}H_{18}Br_3N_3S_2$)				(24.8	3.7	8.7)		
(**6a′**)	77[a]	117—118	$MeCO_2Et$	36.1	5.35	12.6		1 602, 1 552, 1 430, 1 356, 1 215, and 1 060
($C_{10}H_{18}BF_4N_3S_2$)				(36.25	5.5	12.7)		
(**6b**)	34	166—167	MeCN–Et_2O	24.75	3.35	8.65	242	1 602, 1 550, 1 430, 1 330, 1 210, 980, 788, and 595
($C_{10}H_{16}Br_3N_3S_2$				(24.9	3.35	8.7)		
(**15a**)	59	189—190	EtOH	42.9	3.6	8.25		1 605, 1 526, 1 489, 1 442, 1 342, 1 248,
($C_{12}H_{13}Br_4N_2S_2$)				(42.9	3.9	8.35)		1 040, 936, 910, 778, 750, and 660
(**15c**)	41	216—218	EtOH	41.0	3.3	8.0		1 590, 1 525, 1 490, 1 440, 1 358, 1 262,
($C_{12}H_{13}BF_4N_2OS_2$)				(40.9	3.7	8.0)		1 230, 1 050, 912, 778, 740, and 660
(**16a**)	77	160—161	EtOH	39.1	3.35	7.1	283, 285	1 595, 1 526, 1 490, 1 448, 1 354, 1 251,
($C_{12}H_{12}BCl F_4N_2S_2$)				(38.9	3.25	7.5)		1 060, 935, 837, and 660
(**16b**)	32	203—204	EtOH	40.5	3.7	7.4	299,301	1 590, 1 530, 1 489, 1 448, 1 266, 1 065,
($C_{13}H_{14}BCl F_4N_2S_2$)				(40.6	3.65	7.3)		936, 848, and 660
(**16c**)	90	227	EtOH	37.45	3.15	7.3		1 595, 1 580, 1 525, 1 490, 1 443, 1 277,
($C_{12}H_{12}BCl F_4N_2OS_2$)				(37.3	3.1	7.25)		1 254, 1 120, 1 060, 945, 835, and 660
(**16d**)	53	184—185	EtOH	34.6	3.1	8.4		1 622, 1 595, 1 533, 1 491, 1 259, 1 060,
($C_{10}H_{10}BCl F_4N_2S_2$)				(34.85	2.9	8.15)		935, 840, and 660
(**16e**)	11	130.5—131	EtOH	38.35	3.8	7.6		1 585, 1 530, 1 489, 1 351, 1 254, 1 060,
($C_{12}H_{14}BCl F_4N_2S_2$)				(38.65	3.75	7.5)		942, 857, and 662
(**17a**)	30	215—217	EtOH	37.6	3.0	10.9	294	1 608, 1 539, 1 484, 1 356, 1 346, 1 254,
($C_{12}H_{12}BF_4N_3O_2S_2$)				(37.8	3.15	11.0)		1 060, 976, 872, 745, 713, and 683
(**17b**)	43	255	EtOH	39.2	3.45	10.9	308	1 600, 1 545, 1 534, 1 445, 1 365, 1 348,
($C_{13}H_{14}BF_4N_3O_2S_2$)				(39.5	3.55	10.6)		1 253, 1 060, 973, 860, 747, 706, and 682
(**17c**)	86	206—207	MeCN–Et_2O	36.25	2.55	10.55		1 598, 1 541, 1 485, 1 451, 1 361, 1 345,
($C_{12}H_{12}BF_4N_3O_3S_2$)				(36.3	3.0	10.6)		1 280, 1 255, 1 110, 1 060, 975, 875, and 746
(**17d**)	36	219—220	MeOH	33.55	3.05	11.5		1 620, 1 542, 1 530, 1 358, 1 342, 1 245,
($C_{10}H_{10}BF_4N_3O_2S_2$)				(33.8	2.8	11.8)		1 060, 912, 741, 703, and 679

Table 2. (*continued*)

Compound (Formula)	Yield (%)	M.p. (°C)	Solvent	Found (%) (Requires) C	H	N	$M^{+\cdot}$	$\nu_{max.}$ (Nujol/cm^{-1}
(**17e**)	62	183	MeOH	37.6	3.9	10.95		1 591, 1 541, 1 528, 1 464, 1 357, 1 344,
($C_{12}H_{14}BF_4N_3O_2S_2$)				(37.6	3.65	10.95)		1 244, 1 060, 905, 738, 701, and 673
(**18a**)	73	184—186	EtOH	38.0	3.1	10.95	294	1 599, 1 538, 1 522, 1 495, 1 454, 1 355,
($C_{12}H_{12}BF_4N_3O_2S_2$)				(37.8	3.15	11.0)		1 235, 1 055, 959, 881, 855, and 659
(**18b**)	45	193—194	EtOH	39.65	3.75	10.65		1 591, 1 533, 1 522, 1 451, 1 352, 1 331,
($C_{13}H_{14}BF_4N_3O_2S_2$)				(39.5	3.55	10.65)		1 250, 1 055, 941, 870, 850, and 659
(**18c**)	58	278	MeCN–Et_2O	36.35	2.75	10.7		1 587, 1 537, 1 525, 1 492, 1 450, 1 354,
($C_{12}H_{12}BF_4N_3O_3S_2$)				(36.3	3.0	10.6)		1 277, 1 265, 1 112, 1 070, 945, 870, 853, and 662
(**18d**)	65	176	EtOH	34.05	2.95	12.25		1 609, 1 539, 1 525, 1 492, 1 377, 1 360,
($C_{10}H_{10}BF_4N_3O_2S_2$)				(33.8	2.80	11.85)		1 253, 1 055, 940, 875, 853, and 660
(**18e**)	36	201	EtOH	37.9	3.6	11.05		1 588, 1 534, 1 523, 1 471, 1 455, 1 355,
($C_{12}H_{14}BF_4N_3O_2S_2$)				(37.6	3.65	10.95)		1 326, 1 251, 1 060, 947, 874, 856, and 660

[a] From the tribromide (**6a**).

Table 3. ^1H and ^{13}C N.m.r. spectroscopic data for 1,4,2-dithiazolium salts (**6**) and (**15**)—(**18**)

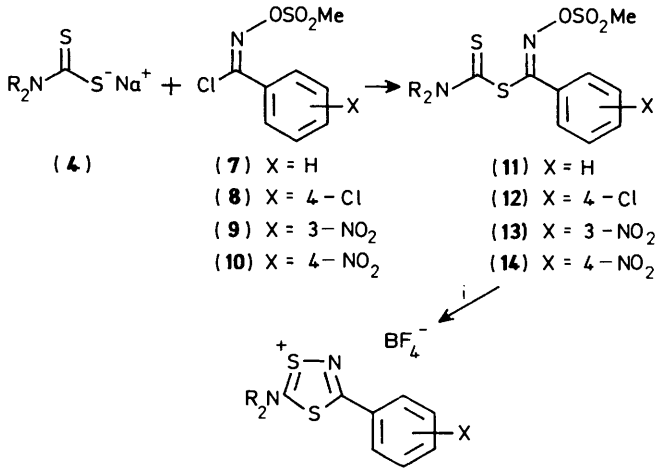
	$\delta_H(CD_3CN)$[a]						$\delta_C(CD_3CN)$[b]								
	3-Aryl			5-NR_2			Ring		3-Aryl				5-NR_2		
Compound	2-, 6-H	3-, 5-H	4-H	α-H	β-H	γ-H	C-3	C-5	C-1	C-2, -6	C-3, -5	C-4	C-α	C-β	C-γ
(**6a**)[c]	3.58[d]	1.32[e]		3.72	2.43		160.68	189.17		47.56[d]	12.95[e]		56.29	26.87	
				4.07									60.46	26.98	
(**6a′**)[c]	3.53[d]	1.27[e]		3.61	2.34		160.62	188.63		47.24[d]	12.68[e]		55.91	26.44	
				3.93									59.81	26.65	
(**6b**)[f]	3.54[d]	2.01[e]		3.60	2.20		157.97	186.74		50.38[d]	25.08[e]		55.75	26.00	
				3.88									59.48	26.22	
(**15a**)	7.95	7.55—7.70		3.71	2.30		168.24	188.56	131.54	130.72	129.15	134.52	58.51	27.20	
				3.87									61.49	27.58	
(**15c**)	7.92	7.53—7.72		3.65—3.95			168.16	196.22	131.54	130.89	129.20	134.73	56.67	65.44	
													59.65	65.71	
(**16a**)[g]	8.02	7.68		3.95	2.42		167.12	188.74	130.55	130.88[h]	130.77[h]	140.09	58.62	27.25	
				4.11									61.54	27.74	
(**16b**)	7.98	7.62		3.74	1.83(br)		166.53	193.84	130.34	130.99[h]	130.67[h]	140.26	59.27	25.52	21.83
				3.91									62.68	25.79	
(**16c**)	7.88	7.63		3.74	3.94		166.91	196.27	130.29	131.05[h]	130.77[h]	140.53	56.77	65.50	
				3.95									59.81	65.77	
(**16d**)	7.88	7.62		3.49			167.61	195.40	130.29	130.99[h]	130.72[h]	140.36	48.70		
				3.63									51.95		
(**16e**)	7.88	7.62		3.79	1.43		167.34	194.43	130.29	130.99[h]	130.72[h]	140.36	56.07	11.00	
				3.91	1.45								58.78		
(**17a**)	8.66	7.86	8.48	3.73	2.32		166.26	188.62	132.83	123.84	150.01	132.45	58.99	27.36	
	8.26			3.88						135.05	128.66		61.92	27.79	
(**17b**)[f]	8.64	7.96	8.54	3.86	1.79(br)		163.77	191.61	131.42	122.32	148.33	131.59	57.97	24.49	20.80
	8.37			4.00						133.92	127.42		61.22	24.70	
(**17c**)	8.66	7.86	8.49	3.77	3.95		165.67	195.89	132.67	123.73	149.85	132.46	56.88	65.44	
	8.26			3.97						135.00	128.66		59.81	65.71	
(**17d**)	8.65	7.85	8.48	3.51			166.42	195.19	132.78	123.73	149.90	132.40	48.87		
	8.25			3.65						135.00	128.61		52.06		
(**17e**)	8.66	7.86	8.48	3.82	1.45		166.15	194.20	132.72	123.73	149.90	132.45	56.29	10.89	
	8.26			3.94	1.46					134.89	128.61		58.89		
(**18a**)	8.12	8.38		3.73	2.32		166.42	188.74	136.52	130.67	125.79	151.58	58.99	27.36	
				3.89									61.92	27.79	
(**18b**)	8.10	8.38		3.77	1.85(br)		165.61	193.67	136.46	130.45	125.79	151.47	59.48	25.52	21.78
				3.95									62.79	25.79	
(**18c**)	8.12	8.40		3.77	3.96		167.07	196.87	136.35	130.61	125.84	151.63	59.92	65.50	
				3.97									63.98	65.77	
(**18d**)	8.11	8.37		3.54			166.58	195.13	136.41	130.56	125.74	151.47	48.86		
				3.67									52.06		
(**18e**)	8.12	8.39		3.81	1.44		166.42	194.37	136.46	130.61	125.90	151.69	56.39	10.94	
				3.93	1.46								58.99		

[a] Digital resolution 0.005 p.p.m. [b] Digital resolution 0.05 p.p.m. [c] In $CDCl_3$. [d] α-Signal of amino substituent. [e] β-Signal of amino substituent. [f] In $(CD_3)_2SO$. [g] In $(CD_3)_2CO$. [h] Assignments uncertain.

corresponding fluoroborate salt (**6a'**). Attempts to extend this method to other analogues of (**6**), having various dialkylamino groups at C-3 and C-5, gave multicomponent solutions containing the required compounds, but from which the products failed to crystallise. However, triethylammonium pyrrolidine-1-dithiocarboxylate gave, with the salt (**3b**) after subsequent treatment with bromine, a moderate yield of the 1,4,2-dithiazolium tribromide (**6b**) (Scheme 3).

While this approach has considerable unexplored potential as a route to these dithiazolium salts, it was not pursued further since an alternative, more attractive, procedure was discovered.

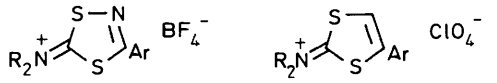
Preparations from α-Chloro Oxime O-Sulphonates.—In the approach shown in Scheme 2, oxidative formation of the S–N bond is no longer necessary if both X and Y are good leaving groups. α-Chloro oxime *O*-sulphonates were known[7] compounds having the desired structural features; examples (**7**)—(**10**) were used in this work. They were found to react with hydrated sodium dithiocarbamates (**4**) in acetone at room temperature to give high yields of isolable intermediates (**11**)—(**14**), most of which were characterised by i.r. and ^{1}H n.m.r. spectroscopy (Table 1), although they were too unstable for satisfactory microanalysis. The dimethylamino and diethylamino compounds showed evidence (n.m.r.) of restricted rotation about the carbamate N–C bond; this feature is also apparent in some closely related compounds.[8] Treatment of the intermediates with fluoroboric acid (54% in ether) gave crystalline precipitates of the novel 1,4,2-dithiazolium salts (**15**)—(**18**) in 11—90% (unoptimised) yields (Scheme 4). We



Scheme 4. *Reagent:* i, HBF_4, Et_2O

thus report a convenient route to 5-amino-1,4,2-dithiazolium salts, which is potentially extendable to 5-alkyl and 5-aryl derivatives if dithiocarboxylate rather than dithiocarbamate salts are used.

Physical, analytical, and i.r. spectroscopic data for 17 examples are in Table 2, and ^{1}H and ^{13}C n.m.r. spectroscopic data are in Table 3. Although parent ions were often absent from their mass spectra, prominent ions corresponding to $R_2N{-}C{\equiv}S^+$ and $ArC{\equiv}N^{+\cdot}$ were always present, and the fragments $R_2NCS_2^{+\cdot}$, $CS_2^{+\cdot}$, and $R_2N^{+\cdot}$ were frequently observed. In the i.r. spectra, prominent common peaks were found near 1 600, 1 530, 1 440, 1 340, and 1 250 cm^{-1}; these were observed also in the salts (**6**), although the last peak was at a somewhat lower frequency. Both ^{1}H and ^{13}C n.m.r. spectra show evidence of restricted rotation about the exocyclic C(5)–N bond, suggesting that the structures might better be represented as (**19**). The ^{1}H n.m.r. spectra of the 1,3-dithiolium salts (**20**)



(**19**) (**20**)

show a similar feature.[9] The NMe_2 ^{1}H n.m.r. signals in the salt (**18d**) coalesce at 158 °C in $(CD_3)_2NCDO$, giving a value of $\Delta G^{\ddagger}$ 95.5 kJ mol^{-1}, a relatively high energy barrier for an iminium group attached to a potentially aromatic ring. In the ^{13}C n.m.r. spectra, the signal for C-3 appears in the range δ 166—168 in CD_3CN; that for C-5 is quite sensitive to the nature of the amino substituent, ranging from δ 189—196. Selected u.v. data are in Table 4, and show some similarities to those for the salts (**20**).[9b]

Crystal Structure Analysis.—The structure of the salt (**18c**) was determined by *X*-ray analysis. The solution of the structure was complicated by disorder in the morpholine moiety, which proved to be present in two different chair conformations. Refinement of the data indicated a ratio of 80:20 for the two forms, and these are shown in Figures 1 and 2 respectively. The

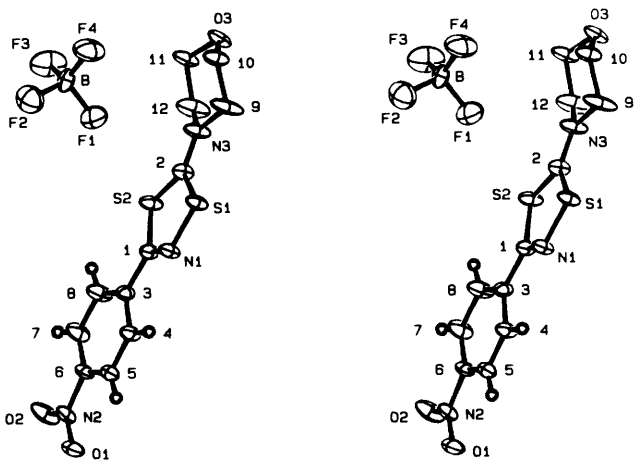


Figure 1. ORTEP drawing of the majority (80%) conformation of the salt (**18c**), showing the non-standard numbering system

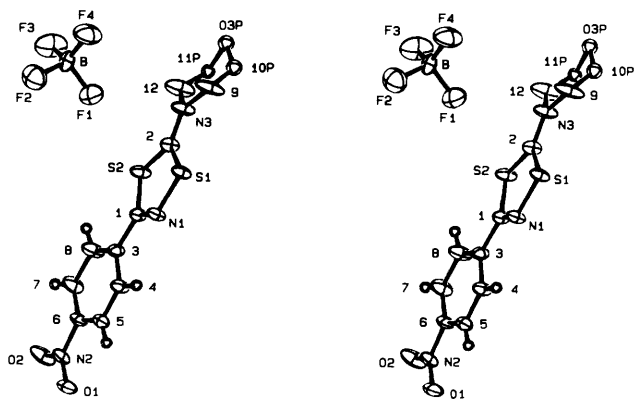


Figure 2. ORTEP drawing of the minority (20%) conformation of the salt (**18c**), showing the non-standard numbering system

Table 4. U.v. spectroscopic data (95% EtOH) for selected dithiazolium salts

Compound	3-Subst.	5-Subst.	$\lambda_{max.}$(log ε)				
(**6a'**)	NEt_2	$N[CH_2]_4$		243 (4.19)			340 (3.78)
(**15a**)	Ph	$N[CH_2]_4$	211 (4.14)	232[a] (4.03)	247 (4.16)	298 (4.03)	
(**16a**)	4-ClC_6H_4	$N[CH_2]_4$	218 (4.22)	242 (4.23)	256 (4.23)	299 (4.20)	304 (4.20)
(**16b**)	4-ClC_6H_4	$N[CH_2]_5$	219 (4.16)	244 (4.19)	255 (4.22)	299 (4.15)	307 (4.16)
(**16c**)	4-ClC_6H_4	$N([CH_2]_2)_2O$	218[a] (4.03)		255 (4.11)	300[a] (4.03)	309 (4.04)
(**16d**)	4-ClC_6H_4	NMe_2	218 (4.13)	242 (4.13)	254 (4.11)	299 (4.10)	303[a] (4.10)
(**16e**)	4-ClC_6H_4	NEt_2	218 (4.05)	244 (4.07)	253 (4.08)	299 (4.04)	305[a] (4.04)
(**17a**)	3-$NO_2C_6H_4$	$N[CH_2]_4$	223[a] (4.27)	241 (4.37)		298 (4.00)	
(**17b**)	3-$NO_2C_6H_4$	$N[CH_2]_5$	213[a] (4.27)	239 (4.43)		286 (4.06)	301 (4.08)
(**18a**)	4-$NO_2C_6H_4$	$N[CH_2]_4$			262 (4.23)	311 (4.08)	

[a] Point of inflection.

Table 5. Selected bond distances and angles for the salt (**18c**) with e.s.d.s in parentheses

a Distances (Å)

S(1)–N(1)	1.660(3)	N(3)–C(9)	1.493(4)
S(1)–C(2)	1.733(3)	N(3)–C(12)	1.494(4)
S(2)–C(1)	1.762(3)	C(1)–C(3)	1.474(4)
S(2)–C(2)	1.727(4)	C(3)–C(4)	1.401(4)
O(1)–N(2)	1.221(4)	C(3)–C(8)	1.384(5)
O(2)–N(2)	1.218(4)	C(4)–C(5)	1.383(5)
O(3)–C(10)	1.442(5)	C(5)–C(6)	1.378(5)
O(3)–C(11)	1.442(5)	C(6)–C(7)	1.373(6)
O(3P)–C(10P)	1.48(2)	C(7)–C(8)	1.391(5)
O(3P)–C(11P)	1.51(2)	C(9)–C(10)	1.477(6)
N(1)–C(1)	1.290(4)	C(9)–C(10P)	1.12(2)
N(2)–C(6)	1.470(5)	C(11)–C(12)	1.488(6)
N(3)–C(2)	1.297(4)	C(11P)–C(12)	1.13(2)

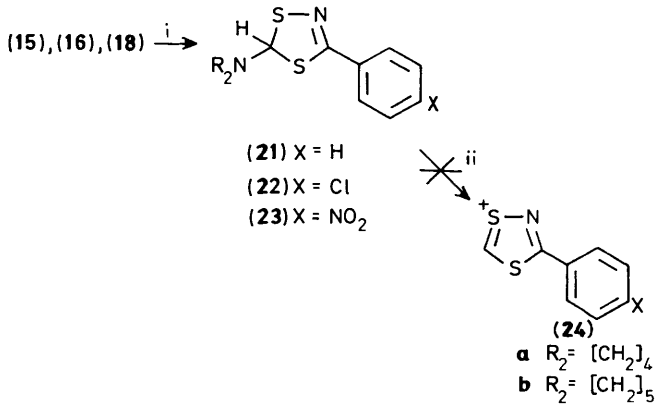
b Angles (°)

N(1)–S(1)–C(2)	98.0(1)	C(1)–C(3)–C(8)	121.9(3)
C(1)–S(2)–C(2)	93.1(2)	C(4)–C(3)–C(8)	119.7(3)
C(10)–O(3)–C(11)	110.4(4)	C(3)–C(4)–C(5)	119.8(3)
C(10P)–O(3P)–C(11P)	107(1)	C(4)–C(5)–C(6)	118.8(3)
S(1)–N(1)–C(1)	116.2(2)	N(2)–C(6)–C(5)	118.1(3)
O(1)–N(2)–O(2)	124.0(2)	N(2)–C(6)–C(7)	119.0(3)
O(1)–N(2)–C(6)	117.8(3)	C(5)–C(6)–C(7)	122.9(4)
O(2)–N(2)–C(6)	118.3(3)	C(6)–C(7)–C(8)	118.0(3)
C(2)–N(3)–C(9)	120.1(3)	C(3)–C(8)–C(7)	120.8(3)
C(2)–N(3)–C(12)	123.2(3)	N(3)–C(9)–C(10)	110.0(3)
C(9)–N(3)–C(12)	115.8(3)	N(2)–C(9)–C(10P)	114.2(9)
S(2)–C(1)–N(1)	119.5(2)	O(3)–C(10)–C(9)	110.9(4)
S(2)–C(1)–C(3)	119.0(2)	O(3P)–C(10P)–C(9)	122(1)
N(1)–C(1)–C(3)	121.5(3)	O(3)–C(11)–C(12)	111.2(4)
S(1)–C(2)–S(2)	113.3(2)	O(3P)–C(11P)–C(12)	114(1)
S(1)–C(2)–N(3)	123.7(2)	N(3)–C(12)–C(11)	110.8(3)
S(2)–C(2)–N(3)	123.1(2)	N(3)–C(12)–C(11P)	116.6(8)
C(1)–C(3)–C(4)	118.4(3)		

large thermal elipsoids associated with N(3), and to a greater extent with C(9) and C(12), are also a consequence of this disorder, and render uncertain some bond parameters associated with these atoms, especially in the minority conformation.

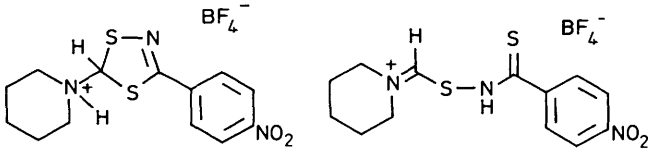
The gross structure is seen to be as predicted, with the atoms making up the dithiazolium moiety all lying within 0.01 Å of the ring mean plane, and N(3) and C(3) being respectively within 0.02 and 0.04 Å of the same plane. The dihedral angle between the dithiazolium and benzene rings is 9(4)°. Selected bond distances and angles are in Table 5; these reveal that N(3)–C(2) (1.297 Å) has considerable double-bond character, while the C–S bonds are all significantly longer than in thiophenes, thiazoles, or isothiazoles. This suggests that most of the positive charge of the cation lies on the exocyclic nitrogen atom, consistent with the rather large energy barrier to rotation for the dimethylamino group in the analogue (**18d**).

Reactions.—We report here only some preliminary results obtained from reactions with selected nucleophiles. 2-Amino-1,3-dithiolium salts of type (**20**) and its analogues are reduced with sodium borohydride in methanol or ethanol to give 2*H*-1,3-dithioles, which on treatment with strong acids form 1,3-dithiolium salts unsubstituted at C-2;[10] these in turn may be converted into tetrathiafulvalenes.[10c] Similar reduction of the salt (**18b**) in ethanol gave a small amount of the 5*H*-1,4,2-dithiazole (**23b**) [δ_H *inter alia* 6.74 (s)], but mostly products resulting from further attack at the ring C=N bond, and from ring cleavage. Reduction below 0 °C in the two-phase system ether/water, however, gave a good yield of compound (**23b**),



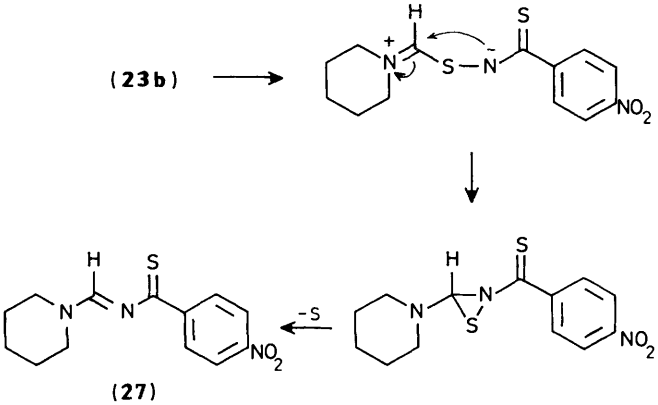
Scheme 5. *Reagents:* i, $NaBH_4$; ii, H^+

which could be isolated and recrystallised, although it decomposed within a few days. Dithiazoles (**21a**), (**22b**), and (**23a**) were prepared similarly in moderate-to-good yields (Scheme 5), n.m.r. signals for 5-H and C-5 being found in the ranges δ_H 6.6—7.0 (s) and δ_C 84—88 (d) respectively. Treatment of compound (**23b**) with 40% aqueous fluoroboric acid, alone or together with acetic anhydride,[11] or with trifluoroacetic anhydride (TFAA) and 54% fluoroboric acid in ether, gave not the expected dithiazolium salt of type (**24**), but a product tentatively assigned as the salt (**25**) on the basis of i.r. and ^{1}H n.m.r. data. The alternative structure (**26**), resulting from protonation of the ring nitrogen followed by ring-opening, was ruled out since (*a*) there was no n.m.r. evidence for restricted rotation about an iminium C=N bond, and (*b*) two low-field singlets [δ_H 7.04 (1 H) and 9.20 (1 H, br)] were more consistent with structure (**25**). Reactions at higher temperatures, or with 70% perchloric acid in ethanol,[10c] resulted in gross decomposition.



(**25**) (**26**)

During attempts to recrystallise the dithiazole (**23b**) from ethanol, it was observed that the boiling solution turned orange-red, and on cooling deposited fine purple plates together with sulphur. The mass spectrum of the purple compound had a molecular ion M^+ 277, suggesting loss of a sulphur atom, and a prominent ion at *m/z* 166 was assigned to the fragment *p*-$NO_2C_6H_4C{\equiv}S^+$. ^{1}H and ^{13}C N.m.r. spectra showed evidence of restricted rotation about the exocyclic bond attached to the piperidine nitrogen atom, which together with the signals δ_H 8.82 (1 H, s) and δ_C 157.97 (d) suggested the structure (**27**), formed as in Scheme 6, and consistent with the microanalytical

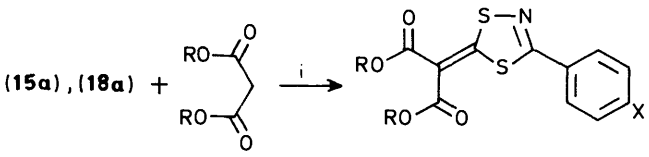


(**27**)

Scheme 6.

data. However, the colour of the compound is somewhat surprising. Further work on products from the dithiazoles (**21**)—(**23**) is underway.

Paton, Crosby, and co-workers reported that 5-methylthio-3-phenyl-1,4,2-dithiazolium fluoroborate reacts with active methylene compounds in the presence of triethylamine, with displacement of the methylthio group and formation of 5-alkylidene derivatives.[2] We find likewise that the amino group is displaced from the 5-pyrrolidino compounds (**15a**) and (**18a**) by the anions of diethyl malonate (**28**) or Meldrum's acid (**29**), formed in the presence of triethylamine (Scheme 7). However,



(**28**) RR = Et_2 (**30**) RR = Et_2 **a** X = H
(**29**) RR = CMe_2 (**31**) RR = CMe_2 **b** X = NO_2

Scheme 7. *Reagent:* i, Et_3N, MeCN

yields of alkylidine derivatives (**30**) and (**31**) appear to be lower by this method; thus we isolated only 31% of compound (**31a**) compared with 53% reported by Paton and Crosby.[2] Reactions of the salts (**15**)—(**18**) with a wide range of nucleophiles are being studied systematically.

Experimental

I.r. spectra were recorded in Nujol on a Perkin-Elmer 157G spectrometer and were calibrated against polystyrene. ^{1}H and ^{13}C N.m.r. spectra were recorded in $CDCl_3$, unless otherwise stated, on a JEOL FX 90Q spectrometer, with Me_4Si as internal reference. Mass spectra were measured on a Hitachi RMS-4 instrument, while that for compound (**6a**) was also recorded on a VG 7070S high-resolution mass spectrometer.

Dithiocarbamates were prepared according to published procedures,[12] and were recrystallised before use. α-Chloro oximes were prepared by chlorination of the appropriate benzaldoximes either directly,[13] or by using *N*-chlorosuccinimide,[14] and converted into the *O*-methanesulphonates (**7**)—(**10**) by the method of Truce and Naik.[7] Preparation of the latter compounds required strictly anhydrous conditions, otherwise products were contaminated with varying amounts of furoxane, derived from dimerisation of the intermediate nitrile oxide.

Bromoformamidinium Bromides (**3**).—*N,N*-Diethylcyanamide (3.4 g, 0.035 mol) was dissolved in anhydrous ether (30 ml), and the solution was treated with dry HBr gas until no more precipitate formed. The mixture was filtered with protection from moisture, and the pale yellow product was washed with ether, and dried to give the bromide (**3a**) (5.9 g, 65%), $\nu_{max.}$ 3 100—2 700 (NH_2^+), 1 645 (NH_2^+), 1 610 (C=N), 1 380, 1 080, and 750 cm^{-1}; δ_H 1.37 (6 H, t), 3.78 (2 H, q), 4.02 (2 H, q), and 10.0 (2 H, br s). The pyrrolidino compound (**3b**) was prepared similarly (90%); $\nu_{max.}$ 3 100—2 700 (NH_2^+), 1 665 (NH_2^+), 1 625 (C=N), 1 385, 1 105, and 710 cm^{-1}; δ_H(CD_3OD), 2.17 (4 H, m), 3.70 (2 H, m), and 3.92 (2 H, m).

3,5-*Diamino*-1,4,2-*dithiazolium Salts* (**6**).—*Compound* (**6a**). Sodium (0.11 g, 4.8 mmol) was dissolved in dry methanol (15 ml), and to the solution were added pyrrolidine (0.4 ml, 4.8 mmol) and carbon disulphide (0.3 ml, 5.0 mmol). The dithiocarbamate solution was cooled to 0 °C, stirred, and treated portionwise with the amidinium bromide (**3a**) (1.15 g, 4.5 mmol), the mixture being stirred for a further 10 min at 7 °C. A solution of bromine in tetrachloromethane (1.5 ml; 1:1) was added dropwise to the cold, stirred solution, whereupon the *dithiazolium tribromide* (**6a**) precipitated as orange plates (0.31 g, 15%); *m/z* 244 (M^+), 114 ($C_4H_8NCS^+$), and 98 ($Et_2NCN^{+\cdot}$). [Analytical data for compounds (**6**) are in Table 2.] Treatment of a solution of the tribromide (200 mg) in dry methanol (1 ml) with cyclohexene (4—5 drops), followed by evaporation and trituration of the residue repeatedly with dry ether, gave a gum which yielded the *fluoroborate salt* (**6a'**) (105 mg, 77%) on treatment with saturated aqueous $NaBF_4$.

Compound (**6b**). Triethylammonium pyrrolidine-1-dithiocarboxylate (1.0 g, 4.03 mmol) was dissolved in dry methanol

(15 ml), and the amidinium bromide (**3b**) (1.04 g, 4.05 mmol) was added portionwise to the cooled (0—4 °C) solution. The mixture was stirred for 2 h, the temperature rising slowly to 20 °C, and the solution was treated with bromine as above, giving the *dithiazolium tribromide* (**6b**) as orange plates.

Preparation of 3-*Aryl*-5-*amino*-1,4,2-*dithiazolium Salts* (**15**)—(**18**).—The synthesis of compound (**18a**) is described; the other salts were prepared similarly. Solutions of the chloro oxime sulphonate (**10**) (1.25 g, 4.48 mmol) and the dithiocarbamate (**4a**) (1.0 g, 4.48 mmol), each in dry, redistilled acetone (30 ml), were mixed at 25 °C and the mixture was stirred for 5 h. The orange-yellow suspension was filtered to remove sodium chloride, and the solvent was evaporated off to give the intermediate (**14a**) (1.3 g, 91%) as a yellow solid. This was dissolved in chloroform (7.5 ml), a solution of fluoroboric acid (54% in ether; 1 ml) was added, and the mixture was stirred for 0.5 h. Dry ether was added slowly to the stirred mixture to precipitate the *product* (**18a**), which was separated by filtration and was recrystallised. Fluoroborate salts could also be prepared by trituration of the intermediates (**11**)—(**14**) directly with fluoroboric acid solution in ether. I.r. and ^{1}H n.m.r. spectroscopic data for the intermediates (**11**)—(**14**) are in Table 1; for intermediate (**13e**), δ_C 11.27q, 13.43q, 37.43q, 49.35t, 49.73t, 125.84d, 129.69d, 135.32s, 148.43s, 155.42s, and 184.62s. Physical, analytical, and spectroscopic data for the salts (**15**)—(**18**) are in Tables 2 and 3.

Rotational Energy Barrier Measurement.—For the dimethylamino compound (**18d**) in $(CD_3)_2NCDO$, the NMe_2 signals (δ_H 3.803 and 3.920; $\Delta\nu$ 10.5 ± 0.4 Hz) coalesced at 431 ± 2 K. From the expression $k_c = \pi\Delta\nu/\sqrt{2}$, and the Eyring equation, $\Delta G^{\ddagger} = 95.5 \pm 0.7$ kJ mol^{-1}.

Reductions with Sodium Borohydride.—The preparation of compound (**23b**) is described. The dithiazolium salt (**18b**) (0.5 g, 1.27 mmol) was suspended in a mixture of water (10 ml) and ether (10 ml), the suspension was stirred and cooled to <0 °C, and sodium borohydride (0.8 g, 21 mmol) was added portionwise. The mixture was stirred for 2 h in the temperature range 0—10 °C, the ether layer was separated, and the aqueous layer was extracted with ether (10 ml). The combined ether layers were dried ($MgSO_4$) and evaporated, and the residue was recrystallised to give 5*H*-1,4,2-dithiazole (**23b**) (0.26 g, 65%) as yellow prisms, m.p. 112 °C; $\nu_{max.}$ 2 790, 1 605, 1 595, 1 520, 1 338, 1 150, and 920 cm^{-1}; δ_H 1.49 (6 H, m), 2.50 (4 H, m), 6.74 (1 H, s), 7.98 (2 H, m) and 8.24 (2 H, m); δ_C 23.84t, 25.30t, 47.48t, 87.87d, 123.89d, 128.99d, 138.63s, 148.49s, and 158.13s; *m/z* 309 (M^+). Prepared similarly were the dithiazole (**21a**) as an oil; $\nu_{max.}$(film) 2 820, 1 593, 1 518, 1 135, and 915 cm^{-1}; δ_H 1.77 (4 H, m), 2.65 (4 H, m), 6.85 (1 H, s), 7.38 (3 H, m), and 7.83 (2 H, m); the dithiazole (**22b**) (47%), m.p. 82 °C (from MeOH); $\nu_{max.}$ 2 820, 1 591, 1 525, 1 161, and 920 cm^{-1}; δ_H 1.48 (6 H, m), 2.50 (4 H, m), 6.67 (1 H, s), 7.38 (2 H, m), and 7.76 (2 H, m); δ_C 23.83t, 25.25t, 47.57t, 87.00d, 128.77d, 129.42d, 131.86s, 136.19s, and 159.38s; and the dithiazole (**23a**) (60%); $\nu_{max.}$ 1 601, 1 595, 1 520, 1 330, 1 135, and 920 cm^{-1}; δ_H 1.80 (4 H, m), 2.64 (4 H, m), 6.98 (1 H, s), 7.98 (2 H, m), and 8.24 (2 H, m); δ_C 24.10t, 47.40t, 83.86d, 123.78d, 128.99d, 138.57s, 148.27s, and 157.48s.

Treatment of the 5H-*Dithiazole* (**23b**) *with Acid.*—The dithiazole (**23b**) (24 mg, 0.078 mmol) was stirred with TFAA (2 ml) at 25 °C, and a solution of fluoroboric acid in ether (54%; 0.5 ml; 0.20 mmol) was added. The white precipitate was filtered off and dried to give the salt (**25**) (23 mg, 72%); $\nu_{max.}$ 3 100, 1 605, 1 595, 1 540, 1 515, 1 400, 1 340, and 1 095 cm^{-1}; δ_H(CF_3CO_2H) 2.00 (6 H, m), 4.07 (4 H, m), 7.04 (1 H, s), 8.10 (2 H, m), 8.36 (2 H, m), and 9.20 (1 H, br s). Reaction of compound (**23b**) in ether with 54% HBF_4, either alone, or together with acetic anhydride, gave the same product.

Rearrangement of the 5H-*Dithiazole* (**23b**).—The dithiazole (**23b**) (50 mg) was heated on a water-bath with 95% ethanol (5.0 ml). The yellow solution turned orange-red and, on cooling, dark purple plates were deposited, together with a small amount of sulphur. The product, m.p. 153—155 °C (from CCl_4), was identified as the *thioacylformamidine* (**27**) (Found: C, 56.1; H, 5.3; N, 15.15. $C_{13}H_{15}N_3O_2S$ requires C, 56.3; H, 5.45; N, 15.15%); $\nu_{max.}$ 1 595vs (C=N), 1 510 and 1 340 (NO_2), 1 440, 1 420, 1 400, 1 325vs, 1 200, 990, 950, 840, and 825 cm^{-1}; δ_H 1.80 (6 H, m), 3.65 (2 H, m), 3.91 (2 H, m), 8.17 (2 H, m), 8.50 (2 H, m), and 8.82 (1 H, s); δ_C 24.00t, 25.30t, 26.71t, 46.32t, 52.93t, 122.76d, 129.42d, 148.50s, 149.41s, 157.97d, and 212.85s; *m/z* 277 (M^+), 244(M^+ − SH), 166 ($O_2NC_6H_4CS^+$), and 84 ($C_5H_{10}N^{+\cdot}$).

Reactions with Malonate Esters.—The preparation of the alkylidenedithiazole (**30a**) is described. The salt (**15a**) (0.20 g, 0.59 mmol) was suspended in acetonitrile (5 ml), and diethyl malonate (0.2 ml, 1.4 mmol) was added, followed by triethylamine (0.5 ml, 5.3 mmol). The solution was stirred at 25 °C for 2 h. The solvent was removed under reduced pressure, and the residue was recrystallised from ethanol to give the *alkylidenedithiazole* (**30a**) (42 mg, 21%), m.p. 128—130 °C (from EtOH) (Found: C, 53.6; H, 4.3; N, 4.2. $C_{15}H_{15}NO_4S_2$ requires C, 53.4; H, 4.5; N, 4.15%); $\nu_{max.}$ 1 665, 1 632, 1 527, 1 408, 1 358, 1 295, 1 280, and 1 020 cm^{-1}; δ_H 1.36 (6 H, t), 4.35 (4 H, 2 q), 7.48 (3 H, m), and 7.94 (2 H, m); δ_C 14.30q, 61.38t, 61.65t, 101.74s, 127.80d, 129.15d, 131.59d, 132.02s, 165.02s, 166.48s and 167.18s; *m/z* 337 (M^+), 234 (M^+ − 103), and 103 ($PhCN^{+\cdot}$).

Similarly were prepared the *dithiazoles* (**30b**) (41%), m.p. 230 °C (from CH_3CN) (Found: C, 47.4; H, 3.9; N, 7.25. $C_{15}H_{14}N_2O_6S_2$ requires C, 47.1; H, 3.7; N, 7.3%); $\nu_{max.}$ 1 668, 1 635, 1 608, 1 535, 1 521, 1 435, 1 360, 1 338, 1 295, 1 190, and 1 015 cm^{-1}; δ_H 1.40 (6 H, t), 4.38 (2 H, q), 4.37 (2 H, q), 8.12 (2 H, m), and 8.34 (2 H, m); δ_C 14.25q, 61.65t, 61.92t, 124.38d, 128.61d, 137.06s, 149.36s, 164.91s, 166.36s, and 167.00s; *m/z* 382 (M^+), 337, and 234; (**31a**) (31%) m.p. 222 °C (from EtOH) (lit.,[2] 222 °C) (Found: C, 52.4, H, 3.45; N, 3.95. Calc. for $C_{14}H_{11}NO_4S_2$: C, 52.3; H, 3.4; N, 4.35%); $\nu_{max.}$ 1 710, 1 676, 1 521, 1 488, 1 440, 1 280, 1 195, and 1 020 cm^{-1}; δ_H 1.75 (6 H, s), 7.44 (3 H, m), and 8.00 (2 H, m); δ_C 27.14q, 93.77s, 105.37s, 128.12d, 129.47d, 131.26s, 132.40d, 160.79s, 162.19s, and 169.18s; *m/z* 321 (M^+) and 103; and (**31b**) (43%), m.p. 280 °C (decomp.) (from CH_3CN) (Found: C, 45.85; H, 2.9; N, 7.8. $C_{14}H_{10}N_2O_6S_2$ requires C, 45.9; H, 2.75; N, 7.65%); $\nu_{max.}$ 1 708, 1 663, 1 608, 1 530, 1 458, 1 340, 1 322, 1 282, 1 183, and 986 cm^{-1}; δ_H[$(CD_3)_2NCDO$; 140 °C] 1.76 (6 H, s), 8.30 (2 H, m), and 8.40 (2 H, m).

Crystal Data for the Dithiazolium Salt (**18c**).—$C_{12}H_{12}BF_4N_3O_3S_2$, M = 397.19, monoclinic, space group $P2_1/c$ (No. 14), Z = 4. At 173 K: a = 7.600(1), b = 14.895(2), c = 14.060(2) Å, β = 101.06(1)°, V = 1 562.1(7) Å^3 (from the setting angles of 50 computer-centred reflections obtained from a crystal measuring 0.22 × 0.15 × 0.46 mm mounted on a Syntex P3 diffractometer), D_c = 1.689 g cm^{-3}. Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 3.88 cm^{-1}. Intensity data were collected using the ω-scan technique, (4° < 2θ < 55°), with scan width 0.29° and scan speed 4.0—10.0° min^{-1}; the ratio of scan time to background counting time was 1.0. A total of 3 588 independent reflections was collected, of which 1 956 with $|F_o| > 3\sigma(|F_o|)$ were used in subsequent calculations. Intensities were corrected for absorption, the variance in the transmission factors being 0.95—1.00.

Solution and refinement. These were carried out as reported elsewhere.[15] The structure was solved using MULTAN and initially refined as an ordered structure including anisotropic

Table 6. Positional parameters for the salt (**18c**), with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
S(1)	0.039 8(2)	0.401 52(9)	0.328 90(9)
S(2)	0.217 8(2)	0.315 96(9)	0.505 83(9)
F(1)	−0.155 2(5)	0.225 4(3)	0.521 2(3)
F(2)	−0.395 2(5)	0.247 1(3)	0.583 3(3)
F(3)	−0.262 6(6)	0.115 4(3)	0.604 6(3)
F(4)	−0.411 3(5)	0.156 2(3)	0.454 9(3)
O(1)	0.644 4(6)	0.724 0(3)	0.777 7(3)
O(2)	0.688 4(6)	0.609 2(3)	0.872 3(3)
O(3)	−0.089 2(6)	0.057 7(3)	0.278 5(3)
O(3P)[a]	0.026(2)	0.069(1)	0.260(1)
N(1)	0.137 8(6)	0.470 8(3)	0.415 5(3)
N(2)	0.621 2(6)	0.645 3(3)	0.796 3(3)
N(3)	0.046 8(6)	0.223 2(3)	0.353 8(3)
C(1)	0.218 3(7)	0.433 8(3)	0.495 0(3)
C(2)	0.091 5(7)	0.301 5(3)	0.391 0(3)
C(3)	0.316 0(7)	0.487 7(3)	0.576 1(3)
C(4)	0.340 0(7)	0.579 4(3)	0.560 9(4)
C(5)	0.437 3(7)	0.631 2(4)	0.634 3(4)
C(6)	0.507 4(7)	0.590 9(4)	0.721 6(4)
C(7)	0.481 7(8)	0.501 8(4)	0.739 9(4)
C(8)	0.386 7(8)	0.449 8(4)	0.665 2(4)
C(9)	−0.054 9(9)	0.215 7(4)	0.252 2(4)
C(10)	−0.181(1)	0.139 5(4)	0.244 1(5)
C(10P)[a]	−0.018(3)	0.156(2)	0.212(2)
C(11)	−0.015(1)	0.064 4(5)	0.380 5(5)
C(11P)[a]	0.165(3)	0.086(2)	0.351(2)
C(12)	0.121 0(9)	0.137 5(4)	0.400 0(4)
B	−0.307 2(8)	0.182 1(5)	0.539 3(4)
H(4)[a]	0.284(8)	0.604(4)	0.496(4)
H(5)[a]	0.458(8)	0.687(4)	0.620(4)
H(7)[a]	0.506(8)	0.483(4)	0.797(4)
H(8)[a]	0.359(8)	0.397(4)	0.680(4)

[a] Refined isotropically.

thermal parameters for all of the non-hydrogen atoms. However, the morpholino group was found to be disordered when a subsequent difference map clearly showed alternative positions for O(3), C(10), and C(11), as well as other peaks which suggested that the anisotropic thermal parameters for atoms N(3), C(9), and C(10) did not adequately represent their electron densities. Further refinements of various disordered models indicated a ratio of 80:20 for the two conformations of the morpholino group. The structural model which was ultimately refined included anisotropic thermal parameters for all of the non-hydrogen atoms of the majority conformation [occupation factors for O(3), C(10), and C(11) were fixed at 0.80], and isotropic thermal parameters for the three morpholino atoms of the minority conformation which were readily distinguished in the difference map [occupation factors for O(3P), C(10P) and C(11P) were fixed at 0.20], and for the hydrogen atoms of the benzene ring (B_{iso} was fixed at 3.0). The full-matrix least-squares refinement converged at $R = 0.058$ and $R_w = 0.060$. The largest peak in the final difference map, 0.63 e Å^{-3}, is undoubtedly representative of a morpholino hydrogen atom. However, not all of the morpholino hydrogens could be located, none refined well, and they were consequently not included in the final cycles of the refinement. Other peaks were found near the fluorine atoms; there may be some slight disordering of the anion, concomitant with that of the morpholine group.

Two crystals of this compound were examined. In both cases, the same degree of disorder was found. Thus disorder appears to be a general feature of the packing for this salt.

Final positional parameters are in Table 6.*

Acknowledgements

We thank Miss Bonnie Yan for recording n.m.r. spectra.

* *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Full lists of bond lengths and angles, and of thermal parameters, together with some least-squares planes, have been deposited at the Cambridge Crystallographic Data centre.

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Received 30*th April* 1987; *Paper* 7/774