Studies of Heterocyclic Compounds. Part XIV.[1] 1,6a-Dithia-6-azapentalenes

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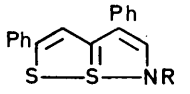
6-Methyl-1,6a-dithia-6-azapentalenes have been synthesised by the reaction of 3-(2-dimethylaminovinyl)-1,2-dithiolium (Vilsmeier) salts or 6a-thiathiophthens with methylamine. 1,6a-Dithia-6-azapentalenes form stable charge-transfer complexes with 1,3,5-trinitrobenzene. The significance of the ^{1}H n.m.r. spectra of 1,6a-dithia-6-azapentalenes is discussed in relation to their structure. 1,6a-Dithia-6-azapentalenes are basic; they form stable 3-(2-methylaminovinyl)-1,2-dithiolium salts with perchloric acid. ^{1}H N.m.r. spectral studies show that protonation of 1,6a-dithia-6-azapentalenes in trifluoroacetic acid occurs predominantly at the nitrogen atom, to form the 3-(2-methylaminovinyl)-1,2-dithiolium cations. The co-existence of low equilibrium concentrations of the corresponding *C*(4)-protonation products with the major products was inferred from the occurrence of H–D exchange in deuteriotrifluoroacetic acid. Exceptionally, 2,5,6-trimethyl-1,6a-dithia-6-azapentalene gave the *N*- and the *C*(4)-protonation product in comparable amounts. Variable temperature ^{1}H n.m.r. spectral studies show that 5-t-butyl- and 5-methyl-3-(2-dimethylaminovinyl)-1,2-dithiolium perchlorate in CD_3CN exist at low temperatures (−20 to −50°) as mixtures of two *trans*-isomers, owing to restricted rotation at the 3,1'- and C(2'),N-bonds. At +60° rapid interconversion of the isomers gives a time-averaged spectrum corresponding to the presence of a single *trans* species. Similar temperature-dependent behaviour was shown by the structurally related 5-t-butyl- and 5-methyl-3-(2-methylaminovinyl)-1,2-dithiolium perchlorates.

CRYSTALLOGRAPHIC studies of the 1,6a-dithia-6-azapentalenes (1)[2] and (2)[3] indicate that their structure and bonding is similar to that in 6a-thiathiophthens. Little is known about this class of compounds apart from the facts that the triphenyl derivative (2) reacts with methyl iodide to give the *S*-methylation product (3)[4] and that acid-catalysed hydrolysis of the derivatives (4)—(6) gives the oxadithiapentalenes (7)—(9), respectively.[5] This paper describes two convenient complementary syntheses of 1,6a-dithia-6-azapentalenes; the formation of charge-transfer complexes; ^{1}H n.m.r. spectral studies of 1,6a-dithia-6-azapentalenes in relation to their structure; studies of their protonation; and variable temperature ^{1}H n.m.r. spectral studies of the geometry of 3-(2-dimethylaminovinyl)-1,2-dithiolium (Vilsmeier) salts in relation to the structure of protonated 1,6a-dithia-6-azapentalenes.

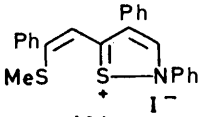
Syntheses, Charge-transfer Complexes, and ^{1}H N.m.r. Spectra of 1,6a-*Dithia*-6-*azapentalenes*.—Three previously described syntheses of 1,6a-dithia-6-azapentalenes have given highly substituted aryl derivatives.[4,5] We required simply substituted compounds for spectral and reactivity studies, and we have developed two syntheses which give, *inter alia*, mono-, di-, and tri-alkyl derivatives. The first method is an extension of the synthesis[6] of 6a-thiathiophthens, 1,6a-dithia-6-selenapentalenes, and 1-oxa-6,6a-dithiapentalenes from 3-(2-dimethylaminovinyl)-1,2-dithiolium (Vilsmeier) salts. Treatment of the Vilsmeier salts (13)—(20) in dimethylformamide with aqueous methylamine gave the dithiaazapentalenes (22)—(29), respectively, in the majority

[1] Part XIII, R. K. Mackie, S. McKenzie, D. H. Reid, and R. G. Webster, *J.C.S. Perkin I*, 1973, 657.
[2] F. Leung and S. C. Nyburg, *Chem. Comm.*, 1969, 137; *Canad. J. Chem.*, 1971, **49**, 167.
[3] F. Leung and S. C. Nyburg, *Canad. J. Chem.*, 1972, **50**, 324.
[4] E. Klingsberg, *J. Org. Chem.*, 1968, **33**, 2915.
[5] H. Behringer and J. Falkenberg, *Chem. Ber.*, 1969, **102**, 1580.
[6] (*a*) J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc.* (*C*), 1968, 2543; (*b*) G. Duguay, D. H. Reid, K. O. Wade, and R. G. Webster, *ibid.*, 1971, 2829; (*c*) J. G. Dingwall, A. R. Dunn, D. H. Reid, and K. O. Wade, *J.C.S. Perkin I*, 1972, 1360; (*d*) J. G. Dingwall, D. H. Reid, and K. O. Wade, *J. Chem. Soc.* (*C*), 1969, 913.

of cases in good yield. Exceptionally, the yield of compound (22) was only 8%. The precursor (13) underwent extensive decomposition during preparation, could not be isolated, and was used *in situ*. In the



(1) R = quinolin-3-yl
(2) R = Ph



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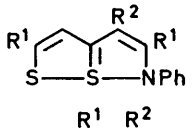
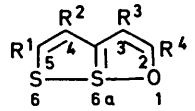
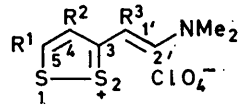


	R¹	R²
(4)	Ph	H
(5)	Me	H
(6)	Ph	CN

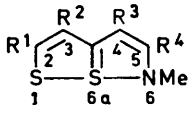


	R¹	R²	R³	R⁴
(7)	Ph	H	H	Ph
(8)	Me	H	H	Me
(9)	Ph	H	CN	Ph
(10)	H	H	H	H
(11)	H	Me	Me	H
(12)	H	Me	Me	Me

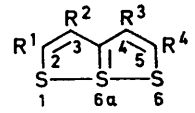


	R¹	R²	R³
(13)	H	H	H
(14)	Bu^t	H	H
(15)	Me	H	H
(16)	H	Me	Me
(17)	H	$[CH_2]_3$	
(18)	Ph	H	H
(19)	Ph	H	Me
(20)	Ph	H	Ph

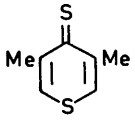
second synthesis the 6a-thiathiophthens (30)—(35) reacted in acetonitrile with ethanolic methylamine to give the dithia-azapentalenes (21)—(23) and (25)—(27),



	R¹	R²	R³	R⁴
(21)	Me	H	H	Me
(22)	H	H	H	H
(23)	Bu^t	H	H	H
(24)	Me	H	H	H
(25)	H	Me	Me	H
(26)	H	$[CH_2]_3$		H
(27)	Ph	H	H	H
(28)	Ph	H	Me	H
(29)	Ph	H	Ph	H



	R¹	R²	R³	R⁴
(30)	Me	H	H	Me
(31)	H	H	H	H
(32)	Bu^t	H	H	H
(33)	H	Me	Me	H
(34)	H	$[CH_2]_3$		H
(35)	Ph	H	H	H



(36)

respectively, in excellent yield. 3,4-Dimethyl-6a-thiathiophthen (33) behaved exceptionally; it gave the thione (36) in addition to the dithia-azapentalene (25). When ethanolic methylamine was used the thione predominated [(25), 26%; (36), 65%], but with aqueous methylamine the dithia-azapentalene (25) became the major product [(25), 66%; (36), 18%]. The thione (36) doubtless arises in a rearrangement [7] of the 6a-thiathiophthen (33) induced by hydrosulphide ion produced in the conversion of the 6a-thiathiophthen into the dithia-azapentalene (25). The part played by the solvent in influencing the ratio of the products (25) and (36) has not yet been established. The first synthesis is preferable in the majority of cases since the Vilsmeier salts are readily available [6] from 3-methyl(ene)-1,2-dithiolium salts, and the corresponding 6a-thiathiophthens required as starting materials in the second synthesis are themselves best obtained [6] from the same Vilsmeier salts. The second synthesis is the method of choice for the preparation of 6-methyl-1,6a-dithia-6-azapentalene (22), whose precursor (31) is best obtained [8] from γ-pyrone, and for the preparation of the 2,5,6-trimethyl derivative (21), whose precursor (30) is readily available from diacetylacetone by Arndt's synthesis.[9] The conversion of the 6a-thiathiophthens (30)—(35) into the corresponding dithia-azapentalenes (21)—(23) and (25)—(27) is an important aspect of the reactivity of 6a-thiathiophthens; it reveals their potential thioaldehyde character.

Stable charge-transfer complexes were obtained from the alkyl 1,6a-dithia-6-azapentalenes (21)—(23), (25), and (26) with 1,3,5-trinitrobenzene. Those from compounds (21)—(23) were red 1 : 1 complexes, whereas the '*peri*'-substituted derivatives (25) and (26) gave a black 2 : 1 and a reddish-black 3 : 2 complex, respectively. The stoicheiometry remained constant irrespective of whether 1 : 1 molecular proportions of reactants were used or an excess of 1,3,5-trinitrobenzene. These are the first reported cases of charge-transfer complex formation involving hypervalent heterocyclic compounds of the 6a-thiathiophthen type as π-donors.[10]

Previously,[6a] on the basis of a comparison of the chemical shifts of protons in 6a-thiathiophthens and 1-oxa-6,6a-dithiapentalenes, we concluded that 6a-thiathiophthens possess larger ring currents and greater aromaticity than 1-oxa-6,6a-dithiapentalenes. The data now available (Table 1) show that the ring protons in 1,6a-dithia-6-azapentalenes are more deshielded than those in the corresponding 1-oxa-6,6a-dithiapentalenes, but much less deshielded than those in the corresponding 6a-thiathiophthens. Thus the ring-proton chemical shifts for 6a-thiathiophthen (31),[6a] 6-methyl-1,6a-dithia-6-azapentalene (22), and 1-oxa-6,6a-dithiapentalene (10) [8] are, respectively, 2-H [≡ 5-H in (10)]: δ 9·18, 8·86, and 7·98; 3-H [≡ 4-H in (10)]: δ 7·96, 7·45, and 7·23; 4-H [≡ 3-H in (10)]: δ 7·96, 7·05, and 6·86. The chemical shifts of substituents in 1,6a-dithia-6-azapentalenes also are intermediate in magnitude between the chemical shifts of substituents in the corresponding 6a-thiathiophthens and those in the corresponding 1-oxa-6,6a-dithiapentalenes. This is exemplified by

[7] J. G. Dingwall and D. H. Reid, *Chem. Comm.*, 1968, 863.
[8] D. H. Reid and R. G. Webster, *J.C.S. Perkin I*, 1972, 1447.
[9] F. Arndt, P. Nachtwey, and J. Pusch, *Ber.*, 1925, **58**, 1633; F. Arndt, E. Aron, C. Martius, and R. Schwarz, *Rev. Fac. Sci. Univ. Istanbul, Ser. A*, 1948, **13**, 57.
[10] D. H. Reid and J. D. Symon, unpublished data.

the series of 3,4-dimethyl derivatives (33),[11] (25), and (11),[11] for which the 3-Me and 4-Me chemical shifts are, respectively, 3-Me [≡ 4-Me in (11)]: δ 2·80, 2·66, and 2·59; 4-Me [≡ 3-Me in (11)]: δ 2·80, 2·52, and 2·47. The progressive increase in deshielding of ring protons

TABLE 1

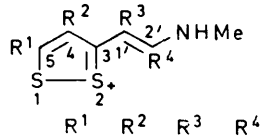
Chemical shifts (δ) in the 100 MHz ^{1}H n.m.r. spectra of the 1,6a-dithia-6-azapentalenes (21)—(29) in $CDCl_3$ (0·4M; 31·4 °C; J in Hz)

	R^1	R^2	R^3	R^4	NMe
(21)	2·55 (d) $J_{2\text{-Me},3}$ 0·7	7·07 (q) $J_{3,2\text{-Me}}$ 0·7	6·76	2·23	3·36
(22)	8·86 (d) $J_{2,3}$ 7·0	7·45 (d) $J_{3,2}$ 7·0	7·05 (d) $J_{4,5}$ 3·4	7·91 (dq) $J_{5,4}$ 3·4 $J_{5,NMe}$ 0·6	3·63 (d) $J_{NMe,5}$ 0·6
(23)	1·38	7·34	6·92 (d) $J_{4,5}$ 3·5	7·85 (dq) $J_{5,4}$ 3·5 $J_{5,NMe}$ 0·6	3·54 (d) $J_{NMe,5}$ 0·6
(24)	2·58	7·20	6·86 (d) $J_{4,5}$ 3·4	7·84 (dq) $J_{5,4}$ 3·4	3·56 (d) $J_{NMe,5}$ 0·6
(25)	8·43 (q) $J_{2,3\text{-Me}}$ 0·8	2·66 (d) $J_{3\text{-Me},2}$ 0·8	2·52 (d) $J_{4\text{-Me},5}$ 0·5	7·67br	3·45 (d) $J_{NMe,5}$ 0·6
(26)	8·34br	*a*	*a*	7·75br	3·59 (d) $J_{NMe,5}$ 0·6
(27)	7·31—7·38(m) [b] 7·80—7·90(m) [c]	7·78	7·04 (d) $J_{4,5}$ 3·6	*ca.* 7·85 [d]	3·58 (d) $J_{NMe,5}$ 0·6
(28)	7·28—7·42(m) [b] 7·81—7·92(m) [c]	7·62	2·29 (d) $J_{4\text{-Me},5}$ 0·5	7·64br	3·54 (d) $J_{NMe,5}$ 0·6
(29)	7·27—7·40(m) [b] 7·70—7·80(m) [c]	7·92	7·43	7·90	3·66

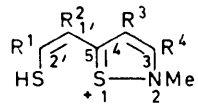
Unless otherwise stated values refer to singlet absorptions. [a] 1·91br (m), 4-H$_2$; 2·76(t), 5-H$_2$; 2·88(t), 3-H$_2$; [b] 2 *m*- + *p*-protons of 2-Ph; [c] 2 *o*-protons of 2-Ph; [d] signal obscured by multiplet from 2 *o*-protons of 2-Ph.

and substituents along the series 1-oxa-6,6a-dithiapentalenes ⟶ 1,6a-dithia-6-azapentalenes ⟶ 6a-thiathiophthens is attributed mainly to a corresponding increase in size of the ring current. We conclude that the extent of π-electron delocalisation in these systems is in the order 6a-thiathiophthens > 1,6a-dithia-6-azapentalenes > 1-oxa-6,6a-dithiapentalenes.

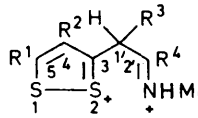
Protonation of 1,6a-*Dithia*-6-*azapentalenes*.—1,6a-Dithia-6-azapentalenes are basic and with perchloric acid give stable perchlorates. Probable sites for protonation are N(6), C(4), and S(1), since protonation at these sites would produce stable heteroaromatic 1,2-dithiolium or isothiazolium cations. The course of protonation was studied by ^{1}H n.m.r. spectroscopy using solutions of the bases in trifluoroacetic acid. Except in the case of the trimethyl compound (21), which will be discussed separately, protonation occurs at N(6) to form the cations (38)—(45). Other protonated species were not present in directly observable amounts. The spectra of 6-methyl-2-t-butyl- (23), 2,6-dimethyl- (24), and 6-methyl-2-phenyl-1,6a-dithia-6-azapentalene (27) show, in addition to the substituent and 3-H signals, an AB pair of doublets (J 12·2 Hz) arising from 1′-H and 2′-H in structures (39), (40), and (43) (Table 2). The presence of the AB system excludes protonation having occurred at C(4). The large 1′-H,2′-H coupling constant is incompatible with *S*-protonation, since this would give a 2,5-disubstituted isothiazolium cation (46) for which a 3-H,4-H [≡ 1′-H,2′-H in structures (38)—(45)] coupling constant of *ca.* 2·6 Hz would be expected (2-methyl- and 2,5-dimethyl-isothiazolium perchlorate show $J_{3,4}$ 2·6 Hz). The spectrum of the cation (38) from 6-methyl-1,6a-dithia-6-azapentalene (22) showed two AB pairs of doublets, at δ 6·41 (1′-H) and 8·15 (2′-H) (J 12·2 Hz) and at δ 7·55 (4-H) and 8·49 (5-H) (J 5·4 Hz). The large 1′-H,2′-H coupling constants indicate a *trans* arrangement for 1′-H and 2′-H in these cations. The NMe signal was not split



	R^1	R^2	R^3	R^4
(37)	Me	H	H	Me
(38)	H	H	H	H
(39)	Bu^t	H	H	H
(40)	Me	H	H	H
(41)	H	Me	Me	H
(42)	H	[CH$_2$]$_3$		H
(43)	Ph	H	H	H
(44)	Ph	H	Me	H
(45)	Ph	H	Ph	H

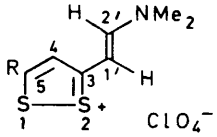


(46)

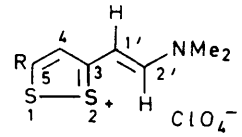


(47)

(47a) R^1 = R^4 = Me, R^2 = R^3 = H



(48a) R = Bu^t
(49a) R = Me



(48b) R = Bu^t
(49b) R = Me

and the NH signal was not observed in the spectra of the cations (37)—(45) owing to proton exchange with the solvent.

The ^{1}H n.m.r. spectrum of the trimethyl derivative (21) in trifluoroacetic acid revealed the presence of the *C*(4)- (47a) and the *N*- (37) protonated species in equilibrium in a 2 : 1 ratio. The spectrum of the cation (47a) shows the two-proton signal of the C(1′)H$_2$ group (δ 5·09) in the expected region. The 4-H signal (δ 8·55) occurs at much lower field than the 4-H signals of the cations (37)—(45); it lies in the range of the 4-H signals of simple alkyl 1,2-dithiolium salts.[6a] The NMe signal (δ 3·57) is also shifted downfield by protonation of the nitrogen atom in the unconjugated methylimino-group.

The presence of the *C*(4)-protonated species (47) in low concentration in equilibrium with the major protonation products (38)—(40) and (43) was established by H–D exchange experiments. The signal due to 4-H in the spectra of the bases (22)—(24) and (27) in trifluoroacetic acid was absent from the spectra of these bases in deuteriotrifluoroacetic acid. Compound (21) also underwent H–D exchange at position 4. The H–D exchange is readily interpreted in terms of a protonation–deprotonation process involving the species (47) as an intermediate.

[11] J. G. Dingwall, D. H. Reid, and J. D. Symon, *J. Chem. Soc.* (*C*), 1970, 2412.

Although there is at present no experimental evidence for *S*-protonation, we think it probable that the cations (46) are also present in low concentration in equilibrium with the *N*(6)- and *C*(4)-protonated species, in view of the fact that 1,6a-dithia-6-azapentalenes undergo kinetically controlled methylation at sulphur [4,10] [*e.g.* (2) ⟶ (3)].

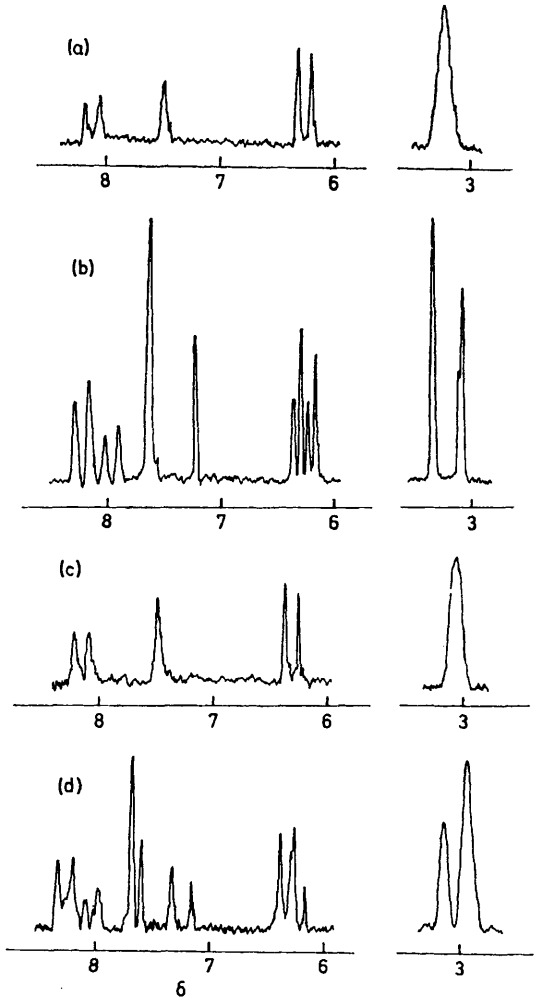
TABLE 2

Chemical shifts (δ) in the 100 MHz ^{1}H n.m.r. spectra of (A) the 3-(2-methylaminovinyl)-1,2-dithiolium cations (37)—(45) [a] and the cation (47a) [a] in trifluoroacetic acid (0·4M; 31·4 °C); (B) the Vilsmeier salts (48) and (49) in CD_3CN (0·15M; various temperatures); and (C) the perchlorates (51) and (52) (0·075 mmol) in CD_3CN (0·5 ml) containing D_2O (40 mg) (various temperatures) (*J* in Hz)

	R^1	R^2	R^3	R^4	NMe
(A)					
(37) [b]	2·66	7·11	6·46	2·56	3·12
(47a) [b]	2·70	8·55	5·09 [c]	3·20	3·57
(38)	8·49 (d)	7·55br (d)	6·41 (d)	8·15br (d)	3·18
	$J_{5,4}$ 5·4	$J_{4,5}$ 5·4	$J_{1',2'}$ 12·2	$J_{2',1'}$ 12·2	
(39)	1·52	7·42	6·26 (d)	8·07 (d)	3·14
			$J_{1',2'}$ 12·2	$J_{2',1'}$ 12·2	
(40)	2·65 (d)	7·34	6·26 (d)	8·07 (d)	3·17
	$J_{5\text{-Me},4}$ 0·9		$J_{1',2'}$ 12·2	$J_{2',1'}$ 12·2	
(41)	8·28 or 8·26	2·61	2·23	8·26 or 8·28	3·36
(42)	8·08 or 8·03	*d*	*d*	8·03 or 8·08	3·38
(43)	7·5—7·8 (m)	7·57	6·35 (d)	8·15 (d)	3·19
			$J_{1',2'}$ 12·2	$J_{2',1'}$ 12·2	
(44)	7·5—7·75 (m)	7·90	2·11	8·26	3·38
(45)	7·30—7·75 (m) [e]	7·94br	7·30—7·75 (m) [e]	8·43br	3·29
(B)					
(48) [f]	1·44	7·48br	6·25 (d)	8·11br(d)	3·23br
			$J_{1',2'}$ 12·4	$J_{2',1'}$ 12·4	
(48) [g]	1·44	*ca.* 7·52vbr	6·26 (d)	*ca.* 8·10 vbr	3·12br 3·35br
(48a) [h]	1·44	7·62	6·24 (d)	8·23 (d)	3·09
			$J_{1',2'}$ 12·4	$J_{2',1'}$ 12·4	3·35
(48b) [h]	1·41	7·23	6·32 (d)	7·96 (d)	3·11
			$J_{1',2'}$ 12·4	$J_{2',1'}$ 12·4	3·35
(49) [f]	2·55 (d)	7·34br	6·23 (d)	8·02 (d)	3·23
	$J_{5\text{-Me},4}$ 0·9		$J_{1',2'}$ 12·4	$J_{2',1'}$ 12·4	
(49) [g]	2·54 (d)	*ca.* 7·30vbr	6·24 (d)	8·00 vbr (d)	3·12 3·33
(49a) [i]	2·53	7·52	6·23 (d)	8·11 (d)	3·09
			$J_{1',2'}$ 12·4	$J_{2',1'}$ 12·4	3·33
(49b) [i]	2·53	7·02	6·27 (d)	7·97 (d)	3·11
			$J_{1',2'}$ 12·4	$J_{2',1'}$ 12·4	3·35
(C)					
(51) [f]	1·44	7·47br	6·31 (d)	8·14 (d)	3·05br
			$J_{1',2'}$ 12·4	$J_{2',1'}$ 12·4	
(51) [h]	1·40 [j]	7·16	*k*	*k*	2·96br
	1·44	7·33			3·16br [l]
		7·60			
		7·67			
(52) [f]	2·56 (d)	7·38br	6·31 (d)	8·09 (d)	3·05br
	$J_{5\text{-Me},4}$ 0·9		$J_{1',2'}$ 12·5	$J_{2',1'}$ 12·5	
(52) [m]	2·50 [n]	7·12	*k*	*k*	2·95br
	2·56	7·27			3·14br [l]
		7·49			
		7·57			

Unless otherwise stated values refer to singlet absorptions. [a] Formed by dissolving the 1,6a-dithia-6-azapentalenes (21)—(29) in trifluoroacetic acid; [b] 0 °C; signals broadened by exchange at 31·4 °C: [c] 1′-H_2; [d] 1·92—2·07br(m), 5-H_2; 2·43(t), 4-H_2; 2·88(t), 6-H_2; [e] 5- + 1′-Ph; [f] 60 °C; [g] 31·4 °C; [h] −20 °C; [i] −50 °C; [j] less intense 5-Bu^t signal; [k] 1′-H and 2′-H signals overlap; [l] less intense NMe signal; [m] −40 °C; [n] less intense 5-Me signal

3-(2-Dimethylaminovinyl)-1,2-dithiolium (Vilsmeier) Salts and Protonated 1,6a-Dithia-6-azapentalenes: Variable Temperature ^{1}H N.m.r. Spectra and Geometry.—A variable temperature ^{1}H n.m.r. spectral study of the structure of the Vilsmeier salts (14) and (15) and of the corresponding salts (39; ClO_4^- counter-ion) and (40; ClO_4^- counter-ion), obtained by treatment of the bases (23) and (24), respectively, with perchloric acid, was carried out. The spectrum of the Vilsmeier salt (14) in CD_3CN at 60° represents a single species [Figure (a)].



100 MHz ^{1}H N.m.r. spectra of 3-(2-dimethylaminovinyl)-5-t-butyl-1,2-dithiolium perchlorate (14) in CD_3CN, (a) at 60°, (b) at −20 °C, and of 3-(2-methylaminovinyl)-5-t-butyl-1,2-dithiolium perchlorate (39; ClO_4^- counter-ion) (0·075 mmol) in CD_3CN (0·5 ml) containing D_2O (40 mg), (c) at 60°, (d) at −20 °C (Bu^t signals not shown)

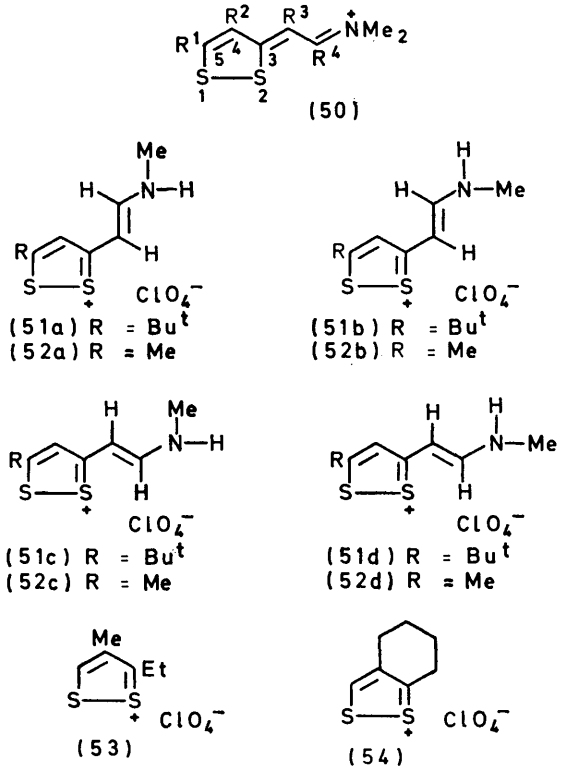
The singlet at δ 3·23 indicates that the NMe groups are equivalent. The 1′-H,2′-H coupling (*J* 12·4 Hz) shows that the 1′,2′-bond is essentially a double bond with 1′-H and 2′-H in a *trans* relationship. On lowering the temperature the NMe_2 singlet broadens, splits, and at normal probable temperature (31·4°) consists of two broad singlets at δ 3·12 and 3·35, corresponding to the

presence of two nonequivalent NMe groups. Over the same temperature fall the 4-H signal and the components of the 2′-H doublet become very broad. Further lowering of temperature results in the emergence of new signals and the sharpening of all signals. At −20° the spectrum [Figure (b)] consists of two superimposed patterns which correspond to the presence of two slowly interconverting species, to which we assign *trans* structures (48a) and (48b) [(48a) : (48b), 5 : 2]. The NMe_2 signal of each species consists of two partly overlapping singlets arising from nonequivalent the NMe groups [(48a), δ 3·09 and 3·35; (48b), δ 3·11 and 3·35]. Two AB systems at low field arise from the 1′-H,2′-H coupling [(48a), δ 6·24 and 8·23; (48b), δ 6·32 and 7·96; $J_{1',2'}$ 12·4 Hz]. The 4-H signals in the two species have markedly different chemical shifts [(48a), δ 7·62; (48b), δ 7·23]. The large 1′-H,2′-H coupling constants (J 12·4 Hz) indicate that in both species the 1′,2′-bond is essentially a double bond with 1′-H and 2′-H in a *trans* relationship. The interconversion barrier is a barrier to free rotation about the 3,1′-bond arising from conjugation between the dithiolium ring and the NMe_2 group. The nonequivalence of the NMe_2 groups, indicative of a rotational barrier at the C(2′),N-bond, also arises from this conjugation. Assignment of the two spectral patterns to structures (48a) and (48b) (Table 2) is based on the interpretation of the 4-H signals and on the intensity relationship of corresponding signals in the two spectral patterns. Thus the anisotropic deshielding of 4-H by the 1′,2′-double bond will be greater in structure (48a) than in structure (48b). The single spectral pattern observed at high temperatures results from a time-averaging effect arising from rapid interconversion of structures (48a) and (48b).

The foregoing n.m.r. spectral data indicate that the 3-(2-dimethylaminovinyl)-1,2-dithiolium formula, for example (48), is a better expression of the structure of the Vilsmeier salts than the 3-methylene-1,2-dithiole formula (50).

5-Methyl-3-(2-dimethylaminovinyl)-1,2-dithiolium perchlorate (15) also exists at low temperatures (−50°) as two interconverting *trans* species (49a) and (49b) [(49a) : (49b), 4 : 3]. The patterns of the low-field regions of the spectra of the two salts (14) and (15) are identical. The signals of the pairs of non-equivalent NMe groups in each of the species (49a) and (49b) are clearly separated. At 60° the spectrum of the salt (15) corresponds to the presence of a single species.

The spectra of the perchlorates obtained by treatment of the dithia-azapentalenes (23) and (24) with perchloric acid were then studied. Since preliminary experiments had indicated that these are *N*-protonated products (39 and 40; ClO_4^- counter-ion) the spectra were obtained using solutions of the perchlorates in CD_3CN containing deuterium oxide, in order to remove the complicating *HNMe* coupling by NH–ND exchange. At 60° the patterns of the spectra of the perchlorates (39; ClO_4^- counter-ion) [Figure (c)] and (40; ClO_4^- counter-ion) were identical with those of the corresponding Vilsmeier salts (14) and (15) in CD_3CN. Also, the chemical shifts of corresponding protons in the pairs of related salts (14), (39; ClO_4^- counter-ion) and (15), (40; ClO_4^- counter-ion) were very similar. The spectrum of the perchlorate (39; ClO_4^- counter-ion) changed in the same manner as that of the Vilsmeier salt (14) upon lowering the temperature. At −20° the spectrum was more complex than that of the Vilsmeier salt (14), although the overall pattern was similar [Figure (d)]. Restricted rotation about the 3,1′- and (2′),N-bonds allows the perchlorates to exist in two pairs of *trans* structures (51a)—(51d) and (52a)—(52d). A comparison of the spectrum of the perchlorate (51) with that of the related Vilsmeier salt (48), both at



−20°, indicates that the major species have the structures (51a) and (51b). Four different 4-H signals occurred, at δ 7·16, 7·33, 7·60, and 7·67 in a ratio *ca.* 2 : 3 : 4 : 6, showing that all four species (51a)—(51d) coexist at low temperatures. Overlapping of signals in the regions δ 6·1—6·4 and 7·9—8·4 prevented assignments from being made to the four AB (1′-H,2′-H) sets of protons. The overlapping NMe signals consisted of two broad signals of unequal intensity at δ 2·96 and 3·16.

Decreasing solubility at low temperatures prevented a well-defined spectrum of the perchlorate (40; ClO_4^- counter-ion) from being recorded. However, at −40°, 4-H signals corresponding to the two pairs of *trans* species (52a)—(52d) were discernible. The close correspondence in spectral pattern, chemical shifts of corresponding protons, and coupling constants in the spectra

of the pairs of salts (14), (39; ClO_4^- counter-ion) and (15), (40; ClO_4^- counter-ion), both at high and low temperatures, establishes that the salts formed by treatment of the 1,6a-dithia-6-azapentalenes with perchloric acid are *N*-protonated products.

3-Ethyl-4-methyl-1,2-dithiolium perchlorate (53), hitherto unknown, was prepared and converted into the corresponding Vilsmeier salt (16) by established procedures.[6] The salt (16) was accompanied by small quantities of 3,4-dimethyl-6a-thiathiophthen (33) and the oxadithiapentalene (12). Compound (12) arises by acetylation–deprotonation of the dithiolium salt (53), but the mode of formation of the 6a-thiathiophthen (33) was not determined. Reaction of the Vilsmeier salt (16) with sodium hydrogen sulphide gave, in addition to 3,4-dimethyl-6a-thiathiophthen (33) (73%), a considerable quantity of the thione (36) (21%) by further reaction of the primary product (33) with the reagent.[6a,7] The Vilsmeier salt (17), previously prepared from the dithiolium salt (54) and used *in situ*,[6c] has now been isolated by a modified procedure; it was also accompanied by a substantial quantity of the corresponding 6a-thiathiophen (34).

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were measured with a Unicam SP 800 spectrophotometer. ^{1}H N.m.r. spectra were determined at 100 MHz with a Varian HA100 spectrometer or at 60 MHz (where indicated) with a Perkin-Elmer R10 spectrometer. Solutions were 0·4M in deuteriochloroform, unless otherwise stated, and tetramethylsilane was used as internal reference; *J* values were measured on the 100 Hz scale. Unless otherwise stated, values refer to singlet absorptions. Solutions were dried over sodium sulphate and evaporated at reduced pressure. Column chromatography was carried out with Spence grade H alumina. Solvent mixtures are described in ratios by volume.

Materials.—Perchloric acid refers to 70—72% (w/w) perchloric acid. Aqueous methylamine was 25—30 (v/v) methylamine; ethanolic methylamine was 33% (w/v) methylamine. Light petroleum was of boiling range 60—80°.

3-Ethyl-4-methyl-1,2-dithiolium Perchlorate (53) *and 4-Methyl-3-(2-dimethylamino-1-methylvinyl)-1,2-dithiolium Perchlorate* (16).—2-Hydroxymethylenepentan-3-one, b.p. 56° at 17 mmHg (lit.,[12] 75—85° at 40—50 mmHg), was prepared (48%) by the method used for 2-hydroxymethylenecyclohexanone.[13] Perchloric acid (6·3 ml, 75 mmol) was added to a solution of 2-hydroxymethylenepentan-3-one (5·7 g, 50 mmol) in acetic acid (100 ml), followed immediately by hydrogen disulphide[14] (3 ml). The solution was heated at 60—65° for 5 min, then cooled, and ether (20 ml) was added. The solution was decanted from precipitated gummy sulphur, then diluted with ether (200 ml). The resulting solid was filtered off and washed with carbon disulphide followed by much ether. *3-Ethyl-4-methyl-1,2-dithiolium perchlorate* (8·52 g, 70%) was obtained as plates (acetic acid), m.p. 97—98°, $\lambda_{max.}$ (AcOH) 304 (log ε 3·83) and 255 nm (3·66), δ ($CF_3{\cdot}CO_2H$; 60 MHz) 1·72 (3H, t, J_{MeCH_2} 7·1 Hz, $MeCH_2$), 2·72 (3H, 4-Me), 3·44 (2H, q, J_{CH_2Me} 7·1 Hz, CH_2Me), and 9·88 (1H, 5-H) (Found: C, 29·2; H, 3·7. $C_6H_9ClO_4S_2$ requires C, 29·4; H, 3·7%).

A mixture of the perchlorate (4·90 g, 20 mmol), dimethylthioformamide[15] (4·2 ml, 50 mmol), and acetic anhydride (60 ml) was boiled for 5 min, cooled, and diluted with ether. *4-Methyl-3-(2-dimethylamino-1-methylvinyl)-1,2-dithiolium perchlorate* (5·00 g, 83%) was obtained after filtration and washing with ether as orange plates (acetonitrile), m.p. 146—149° (Found: C, 36·0; H, 5·0; N, 5·2. $C_9H_{14}ClNO_4S_2$ requires C, 36·0; H, 4·7; N, 4·7%). The red acetic anhydride–ether filtrates were treated with aqueous sodium hydroxide and set aside. The ether layer was washed with water, dried, and evaporated. Chromatography (alumina; 40 × 2·5 cm) of the oily residue with benzene gave crimson eluates from which 3,4-dimethyl-6a-thiathiophthen (33)[11] (195 mg, 5%) was isolated. Continued elution with benzene–ether (3 : 1) brought through an orange band which yielded *2,3,4-trimethyl-1-oxa-6,6a-dithiapentalene* (12) (80 mg, 2%), yellow needles from cyclohexane, m.p. 90—91°, $\lambda_{max.}$ (cyclohexane) 436 (log ε 4·02), 422 (4·05), 274 (3·16), 224 (4·20), and 205 nm (3·98), δ ($CDCl_3$; 60 MHz) 2·34 (3H, 2-Me), 2·44 (3H, 3-Me), 2·58 (3H, d, $J_{4\text{-}Me,5}$ 0·9 Hz, 4-Me), and 7·62br (1H, 5-H) (Found: C, 51·8; H, 5·6. $C_8H_{10}OS_2$ requires C, 51·6; H, 5·4%).

3,4-Dimethyl-6a-thiathiophthen (33) *and 3,5-Dimethylthiopyran-4-thione* (36) *from the Vilsmeier Salt* (16).—Aqueous 2M-sodium hydrogen sulphide (25 ml) was added to a solution of the Vilsmeier salt (16) (1·50 g, 5 mmol) in methanol (40 ml) and acetonitrile (20 ml). The mixture was diluted with water and extracted with benzene. The residue from the washed, dried, and evaporated extracts was chromatographed (alumina; 25 × 3·0 cm) with benzene–light petroleum (2 : 1). The crimson eluates gave 3,4-dimethyl-6a-thiathiophthen (685 mg, 73%), dark red needles from cyclohexane, m.p. 132—133° (lit.,[11] 132—133°), $\lambda_{max.}$ (cyclohexane), 492 (log ε 3·73), 264 (4·69), 236 (4·28), and 205 nm (4·11) (Found: C, 45·0; H, 4·7; S, 51·3. Calc. for $C_7H_8S_3$: C, 44·7; H, 4·3; S, 51·1%). Continued elution with benzene brought through purple eluates which yielded 3,5-dimethylthiopyran-4-thione (164 mg, 21%), red needles from cyclohexane, m.p. 122—123° (lit.,[16] 125—126°), δ ($CDCl_3$; 60 MHz) 2·52 (6H, 3- + 5-Me) and 7·69 (2H, 2- + 6-H), δ ($CF_3{\cdot}CO_2H$; 60 MHz; spectrum of the 4-mercapto-3,5-dimethylthiopyrylium cation) 2·87 (6H, 3- + 5-Me) and 9·20 (2H, 2- + 6-H).

7-Dimethylaminomethylene-4,5,6,7-tetrahydrobenzo[c][1,2]-dithiolium Perchlorate (17).—Phosphoryl chloride (5·5 ml, 60 mmol) was added to a suspension of 4,5,6,7-tetrahydrobenzo[*c*][1,2]dithiolium perchlorate (54)[6c] (5·13 g, 20 mmol) in dimethylthioformamide (25 ml), and the mixture was set aside at room temperature overnight. The red mixture was filtered, and the residue was washed until colourless with dimethylformamide (10 ml) and then with acetonitrile (10 ml) before being discarded. Addition of ether (400 ml) to the combined filtrates precipitated an oil. After decantation of the ether layer the residual oil was dissolved in acetonitrile (30 ml) and treated with

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[13] C. Ainsworth, *Org. Synth.*, 1959, **39**, 27.
[14] F. Feher, W. Laue, and G. Winkhaus, *Z. anorg. Chem.*, 1956, **288**, 113.
[15] G. R. Pettit and L. R. Garson, *Canad. J. Chem.*, 1965, **43**, 2640.
[16] P. Beak and E. M. Monroe, *J. Org. Chem.*, 1969, **34**, 589.

perchloric acid (2·1 ml, 25 mmol). Gradual addition of ether to the resulting solution gave *7-dimethylaminomethylene-4,5,6,7-tetrahydrobenzo*[c][1,2]*dithiolium perchlorate* (4·34 g, 70%), red prisms from ethanol–acetonitrile (9 : 1), m.p. 155—157° (Found: C, 38·7; H, 4·8; N, 4·5. $C_{10}H_{14}ClNO_4S_2$ requires C, 38·6; H, 4·5; N, 4·5%). The decanted red ether layer was washed thrice with water, dried, and evaporated, and the residual oil was chromatographed (silica; 30 × 3·5 cm) with light petroleum–benzene (2 : 1). The red eluates yielded 4,5-dihydro-3*H*-benzo[*cd*][6a]thiathiophthen (34) [6c] (1·02 g, 25%).

Preparation of 1,6a-*Dithia*-6-*azapentalenes from* 3-(2-*Dimethylaminovinyl*)-1,2-*dithiolium* (*Vilsmeier*) *Salts: General Procedure*.—Aqueous methylamine (25 ml) was added to a solution of the Vilsmeier salt (5 mmol) in dimethylformamide (25 ml) at room temperature. After 10 min the mixture was diluted with water and extracted with benzene (×4). The combined extracts were washed with water (×5), dried, and evaporated. The residue was chromatographed (alumina; 45 × 2·7 cm) with benzene. Evaporation of the major yellow or orange band and recrystallisation gave the 1,6a-dithia-6-azapentalene. In several cases the product was preceded by a trace of the corresponding 6a-thiathiophthen and/or succeeded by a small quantity of one or two unidentified yellow compounds; these were discarded.

Charge-transfer complexes of the 1,6a-dithia-6-azapentalenes with 1,3,5-trinitrobenzene were prepared by addition of the base (1 mmol) in hot ethanol (5—10 ml) to a boiling solution of the reagent (1 mmol, unless otherwise stated) in ethanol (5 ml). The composition (in parentheses) was obtained by elemental analysis and checked by integration of the ^1H n.m.r. spectrum (solvent $CDCl_3$).

The following 1,6a-dithia-6-azapentalenes and 1,3,5-trinitrobenzene complexes were obtained: *6-methyl-2-t-butyl*-1,6a-*dithia*-6-*azapentalene* (23) (970 mg, 91%) [from the salt (14) [6d]], greenish-yellow needles from hexane, m.p. 122—123°, $\lambda_{max.}$ (MeOH) 414 (log ε 4·09), 265sh (3·74), 233 (4·28), and 213 nm (4·06) (Found: C, 56·5; H, 7·3; N, 6·6. $C_{10}H_{15}NS_2$ requires C, 56·3; H, 7·1; N, 6·6%); *trinitrobenzene complex* of (23) (1 : 1) (87%), red plates, m.p. 113—114° (decomp.) (Found: C, 45·4; H, 4·5; N, 13·4. $C_{16}H_{18}N_4O_6S_2$ requires C, 45·1; H, 4·3; N, 13·1%); 2,6-*dimethyl*-1,6a-*dithia*-6-*azapentalene* (24) (650 mg, 76%) [from the salt (15) [6a]], yellow spars from hexane, m.p. 136—137°, $\lambda_{max.}$ (MeOH) 414 (log ε 4·14), 265sh (3·82), 234 (4·46), and 209 nm (4·17) (Found: C, 49·2; H, 5·5; N, 8·0. $C_7H_9NS_2$ requires C, 49·1; H, 5·3; N, 8·2%); 3,4,6-*trimethyl*-1,6a-*dithia*-6-*azapentalene* (25) (666 mg, 72%) [from the salt (16)], yellow needles from hexane, m.p. 132—133°, $\lambda_{max.}$ (MeOH) 433 (log ε 4·03), 268infl (3·77), 243 (4·42), and 209 nm (4·06), $\lambda_{max.}$ (cyclohexane) 436 (log ε 4·04), 269infl (3·71), 238 (4·35), and 209 nm (4·21) (Found: C, 52·1; H, 6·1; N, 7·4. $C_8H_{11}NS_2$ requires C, 51·9; H, 6·0; N, 7·6%); *trinitrobenzene complex* of (25) (2 : 1) (86%), black needles, m.p. 150—152° (decomp.) (Found: C, 45·5; H, 4·5; N, 12·0. $C_{22}H_{25}N_5O_6S_4$ requires C, 45·3; H, 4·3; N, 12·0%); 4,5-*dihydro*-7-*methyl*-3H-*benzo*[cd]-1,6a-*dithia*-6-*azapentalene* (26) (890 mg, 90%) [from the salt (17)], orange needles from acetonitrile, m.p. 95—95·5°, $\lambda_{max.}$ (MeOH) 434 (log ε 4·03), 270infl (3·73), 237 (4·48), and 211 nm (4·06), $\lambda_{max.}$ (cyclohexane) 438 (log ε 3·99), 274infl (3·62), 246sh (4·18), 229 (4·29), and 209sh nm (4·17) (Found: C, 54·7; H, 5·6; N, 7·1. $C_9H_{11}NS_2$ requires C, 54·8; H, 5·6; N, 7·1%); *trinitrobenzene complex* of (26) (3 : 2) (93%; prepared with 0·5 mmol reagent), reddish-black needles, m.p. 123—125° (decomp.) (Found: C, 46·4; H, 4·1; N, 12·2. $C_{39}H_{39}N_9O_{12}S_6$ requires C, 46·0; H, 3·9; N, 12·4%); 6-*methyl*-2-*phenyl*-1,6a-*dithia*-6-*azapentalene* (27) (1·07 g, 92%) [from the salt (18) [6a]], yellow needles from acetonitrile, m.p. 155—157°, $\lambda_{max.}$ (MeOH) 435 (log ε 4·19), 289br (4·02), and 234 nm (4·50) (Found: C, 61·8; H, 4·9; N, 6·1. $C_{12}H_{11}NS_2$ requires C, 61·8; H, 4·8; N, 6·0%); (with S. McKenzie) 4,6-*dimethyl*-2-*phenyl*-1,6a-*dithia*-6-*azapentalene* (28) (1135 mg, 92%) [from the salt (19) [6a]], orange spars from acetonitrile, m.p. 175—176°, $\lambda_{max.}$ (MeOH) 442 (log ε 4·19), 284br (4·02), and 236 nm (4·52) (Found: C, 62·8; H, 5·6. $C_{13}H_{13}NS_2$ requires C, 63·1; H, 5·3%); 6-*methyl*-2,4-*diphenyl*-1,6a-*dithia*-6-*azapentalene* (29) (1400 mg, 91%) [from the salt (20) [6a]], orange spars from acetonitrile, m.p. 173—173·5°, $\lambda_{max.}$ (MeOH) 447 (log ε 4·24), 280br (4·18), and 236 nm (4·52) (Found: C, 69·5; H, 4·8. $C_{18}H_{15}NS_2$ requires C, 69·5; H, 4·9%).

6-*Methyl*-1,6a-*dithia*-6-*azapentalene* (22) *from* 3-*Methyl*-1,2-*dithiolium Perchlorate*.—A mixture of 3-methyl-1,2-dithiolium perchlorate [6a] (4·34 g, 20 mmol), dimethylthioformamide (8·4 ml, 100 mmol), and acetic anhydride (80 ml) was boiled for 5 min. Acetic anhydride was distilled off at 15 mmHg, and the residual black oil was washed with ether, dissolved in dimethylformamide, and treated with aqueous methylamine (50 ml). The resulting mixture was diluted with water and extracted with ether. The extracts were washed with water, dried, and evaporated, and the residue was chromatographed (alumina; 20 × 3·0 cm) with benzene. The yellow eluates afforded 6-*methyl*-1,6a-*dithia*-6-*azapentalene* (255 mg, 8%), yellow needles from hexane, m.p. 107—108°, $\lambda_{max.}$ (MeOH) 415 (log ε 4·08), 263sh (3·89), 235 (4·46), and 208 nm (4·15), $\lambda_{max.}$ (cyclohexane) 418 (log ε 3·99), 261sh (3·68), 232 (4·31), and 214 nm (4·20) (Found: C, 45·8; H, 4·6; N, 9·0. $C_6H_7NS_2$ requires C, 45·8; H, 4·5; N, 8·9%); *trinitrobenzene complex* (1 : 1) (76%), red needles, m.p. 111—112° (decomp.) (Found: C, 39·2; H, 2·8; N, 15·0. $C_{12}H_{10}N_4O_6S_2$ requires C, 38·9; H, 2·7; N, 15·1%).

Preparation of 1,6a-*Dithia*-6-*azapentalenes from* 6a-*Thiathiophthens*.—The following general procedure was used (deviations are given in individual cases). Ethanolic methylamine (25 ml) was added to a solution of the 6a-thiathiophthen (5 mmol) in acetonitrile (150 ml) at 60°. The mixture was stirred at this temperature for 40 min before being diluted with water and extracted with benzene (×4). The combined extracts were washed with water, dried, and evaporated, and the residue was chromatographed (alumina; 45 × 2·7 cm) with benzene. The following 1,6a-dithia-6-azapentalenes were obtained: 6-methyl-2-t-butyl-1,6a-dithia-6-azapentalene (23) (860 mg, 80%) [from 2-t-butyl-6a-thiathiophthen (32) [6b]], yellow needles from hexane, m.p. 122—123°; 4,5-dihydro-7-methyl-3*H*-benzo[*cd*]-1,6a-dithia-6-azapentalene (26) (940 mg, 96%) {from 4,5-dihydro-3*H*-benzo[*cd*][6a]thiathiophthen (34) [6c]}; 6-methyl-2-phenyl-1,6a-dithia-6-azapentalene (27) (895 mg, 75%) [from 2-phenyl-6a-thiathiophthen (35) [6a]].

2,5,6-*Trimethyl*-1,6a-*dithia*-6-*azapentalene* (21) *from* 2,5-*dimethyl*-6a-*thiathiophthen* (30). Ethanolic methylamine (25 ml) was added to a solution of 2,5-dimethyl-6a-thiathiophthen [9] (940 mg, 5 mmol) in acetonitrile (150 ml) at 60°. The mixture was stirred at this temperature for 20 min, more ethanolic methylamine (25 ml) was added, and

stirring was continued for a further 20 min at 60°. The solution was diluted with water and extracted with benzene (×5). The residue from the washed, dried, and evaporated extracts was chromatographed (alumina; 45 × 2·7 cm) with benzene. The initial orange eluates contained a small quantity of starting material. The succeeding yellow eluates afforded 2,5,6-*trimethyl*-1,6a-*dithia*-6-*azapentalene* (684 mg, 74%), yellow plates from cyclohexane, m.p. 144—145°, $\lambda_{max.}$ (MeOH) 414 (log ε 3·95), 263sh (3·89), 237 (4·24), and 214infl nm (4·05) (Found: C, 52·1; H, 6·3; N, 7·9. $C_8H_{11}NS_2$ requires C, 51·9; H, 6·0; N, 7·6%); *trinitrobenzene complex* (1 : 1) (85%), red needles, m.p. 143—144° (decomp.) (Found: C, 42·2; H, 3·6; N, 14·2. $C_{14}H_{14}N_4O_6S_2$ requires C, 42·4; H, 3·5; N, 14·1%).

6-*Methyl*-1,6a-*dithia*-6-*azapentalene* (22) *from* 6a-*thiathiophthen* (31). Aqueous methylamine (25 ml) was added to a solution of 6a-thiathiophthen [8] (800 mg, 5 mmol) in acetonitrile (150 ml) at room temperature. After 5 min the solution, which had become dark and then light red, was diluted with water and extracted with ether. The extracts were washed with water (×3), dried, and evaporated. Chromatography (alumina; 20 × 2·5 cm) of the residue with benzene gave orange eluates containing a trace of starting material, and subsequently yellow eluates which afforded 6-methyl-1,6a-dithia-6-azapentalene (710 mg, 90%), yellow needles from cyclohexane–benzene (1 : 1), m.p. 108—109°.

3,4,6-*Trimethyl*-1,6a-*dithia*-6-*azapentalene* (25) *and* 3,5-*dimethylthiopyran*-4-*thione* (36) *from* 3,4-*dimethyl*-6a-*thiathiophthen* (33). (*a*) Aqueous methylamine (25 ml) was added to a solution of 3,4-dimethyl-6a-thiathiophthen (940 mg, 5 mmol) in acetonitrile (150 ml) at 60°. The mixture was stirred at this temperature for 20 min before being diluted with water and worked up according to the general procedure. Chromatography (alumina; 50 × 2·7 cm) of the residue with benzene gave purple eluates which yielded 3,5-dimethylthiopyran-4-thione (134 mg, 18%), and subsequently yellow eluates which afforded 3,4,6-trimethyl-1,6a-dithia-6-azapentalene (614 mg, 66%).

(*b*) The general procedure was used. The product was chromatographed (alumina; 50 × 2·7 cm) with light petroleum–benzene (2 : 1), which removed a small quantity of starting material, and subsequently with benzene which brought through successively 3,5-dimethylthiopyran-4-thione (505 mg, 65%) and 3,4,6-trimethyl-1,6a-dithia-6-azapentalene (240 mg, 26%).

Preparation of 3-(2-*Methylaminovinyl*)-1,2-*dithiolium Perchlorates from* 1,6a-*Dithia*-6-*azapentalenes*.—Perchloric acid (0·1 ml, 1·2 mmol) was added to a solution of the 1,6a-dithia-6-azapentalene (1 mmol) in acetonitrile (10 ml). Gradual addition of ether precipitated the perchlorate. Recrystallisation was from acetonitrile containing 2% (v/v) perchloric acid, unless otherwise stated. The following salts were obtained: 5-*methyl*-3-(2-*methyl*-2-*methylaminovinyl*)-1,2-*dithiolium perchlorate* (37; ClO_4^- counter-ion) (96%), yellow needles from methanol containing 2% (v/v) perchloric acid, m.p. 146—147° (Found: C, 33·9; H, 4·4; N, 5·1. $C_8H_{12}ClNO_4S_2$ requires C, 33·6; H, 4·2; N, 4·9%); 3-(2-*methylaminovinyl*)-1,2-*dithiolium perchlorate* (38; ClO_4^- counter-ion) (90%), yellow needles,* m.p. 139—140° (Found: C, 28·0; H, 3·1; N, 5·3. $C_6H_8ClNO_4S_2$ requires C, 28·0; H, 3·1; N, 5·4%); 3-(2-*methylaminovinyl*)-5-*t*-*butyl*-1,2-*dithiolium perchlorate* (39; ClO_4^- counter-ion) (84%), green needles, m.p. 154—155° (decomp.) (Found: C, 38·2; H, 5·3; N, 4·3. $C_{10}H_{16}ClNO_4S_2$ requires C, 38·3; H, 5·2; N, 4·5%); 5-*methyl*-3-(2-*methylaminovinyl*)-1,2-*dithiolium perchlorate* (40; ClO_4^- counter-ion) (78%), orange needles, m.p. 124—125° (Found: C, 30·8; H, 3·8; N, 5·1. $C_7H_{10}ClNO_4S_2$ requires C, 30·9; H, 3·7; N, 5·2%); 4-*methyl*-3-(1-*methyl*-2-*methylaminovinyl*)-1,2-*dithiolium perchlorate* (41; ClO_4^- counter-ion) (98%), yellow needles, m.p. 229—231° (Found: C, 33·3; H, 4·2; N, 4·6%); 4,5,6,7-*tetrahydro*-7-*methylaminomethylenebenzo*[c]-[1,2]*dithiolium perchlorate* (42; ClO_4^- counter-ion) (99%), red needles, m.p. 194—196° (Found: C, 36·3; H, 4·2; N, 4·9. $C_9H_{12}ClNO_4S_2$ requires C, 36·3; H, 4·2; N, 4·9%); 3-(2-*methylaminovinyl*)-5-*phenyl*-1,2-*dithiolium perchlorate* (43; ClO_4^- counter-ion) (91%), red needles, m.p. 157—157·5° (Found: C, 42·7; H, 3·7; N, 4·1. $C_{12}H_{12}ClNO_4S_2$ requires C, 43·0; H, 3·6; N, 4·2%).

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* Attempted recrystallisation resulted in decomposition.