Studies of Heterocyclic Compounds. Part XV.[1] Synthesis and Structure of 6a-Thia-1,6-diazapentalenes (Isothiazolo[5,1-*e*]isothiazoles)[2]

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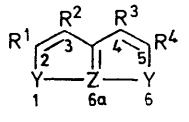
Methylation of 6-methyl-1,6a-dithia-6-azapentalenes with methyl iodide occurs exclusively at sulphur (S-1). The resulting 2-methyl-5-(2-methylthiovinyl)isothiazolium iodides react with methylamine to give symmetrical 6a-thia-1,6-diazapentalenes, a new class of hypervalent heterocyclic compound. 4,5-Dihydro-1,7-dimethyl-3*H*-benzo[*cd*]-6a-thia-1,6-diazapentalene and 1,2,5,6-tetramethyl-6a-thia-1,6-diazapentalene were accompanied by small quantities of thiones which result from reductive cleavage of the S–N bond in the 2-methyl-5-(2-methylthiovinyl)isothiazolium cations. 1,6-Dimethyl- and 1,3,4,6-tetramethyl-6a-thia-1,6-diazapentalene were accompanied by the corresponding 6-methyl-1,6a-dithia-6-azapentalenes formed by *S*-demethylation of the 2-methyl-5-(2-methylthiovinyl)isothiazolium cations. ^{1}H N.m.r. spectral studies show that symmetrically substituted 6a-thia-1,6-diazapentalenes in solution possess real or time-averaged C_{2v} symmetry. The pattern of the spectrum of 1,3,4,6-tetramethyl-6a-thia-1,6-diazapentalene was unaffected by change of solvent [$CDCl_3$, CS_2, or $(CD_3)_2SO$] or by lowering the temperature of a solution in CS_2 to −70°. The significance of the ^{1}H n.m.r. spectra of 6a-thia-1,6-diazapentalenes and analogues of 6a-thiathiophthens is discussed in relation to structure. 6a-Thia-1,6-diazapentalenes form stable charge-transfer complexes with 1,3,5-trinitrobenzene.

In previous papers[2,3] we expressed our intention to synthesise and study heterocyclic systems based on structure (1), in which Y and Z are heteroatoms of Groups V and VI and Z is a second or lower row element theoretically capable of valence-shell expansion. This paper describes a synthesis and spectral studies pertinent to the structure of 6a-thia-1,6-diazapentalenes (1; Y = NMe, Z = S), a novel class of hypervalent heterocyclic compound structurally analogous to 6a-thiathiophthen (1; Y = Z = S).



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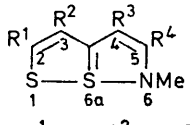
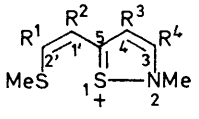


	R^1	R^2	R^3	R^4
(2)	H	H	H	H
(3)	H	Me	Me	H
(4)	H	$[CH_2]_3$		H
(5)	Me	H	H	Me



X⁻ (6a)–(9a) X = I; (6b)–(9b) X = ClO_4

	R^1	R^2	R^3	R^4
(6)	H	H	H	H
(7)	H	Me	Me	H
(8)	H	$[CH_2]_3$		H
(9)	Me	H	H	Me

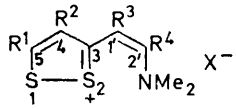
Our initial synthetic objectives were symmetrically substituted 6a-thia-1,6-diazapentalenes whose anticipated C_{2v} symmetry would be advantageous in spectral, theoretical, and crystallographic studies. The 1,6a-dithia-6-azapentalenes (2)—(5)[1] reacted rapidly and quantitatively with methyl iodide in acetonitrile to give the yellow isothiazolium iodides (6a)—(9a). The ^{1}H n.m.r. spectra [$(CD_3)_2$)SO] of the iodides and the corresponding perchlorates, prepared by treatment of the iodides with 70% perchloric acid, are consistent with the *S*-methyl structures (6)—(9); they show only one NMe signal in the δ 4—4·4 region but display an SMe signal at considerably higher field (δ 2·4—2·9). The fact that the perchlorates (7b) and (8b) are different from the known Vilsmeier perchlorates (12)[1,2] and (13)[1] shows that *N*-methylation had not occurred. The possibility of methylation at C-3 or C-4 is also discounted by the absence of a methylene or substituted methylene signal in the δ 4—5·5 region. Methylation of the 1,6a-dithia-6-azapentalenes (2)—(5) thus takes place under kinetic control at sulphur (S-1), in contrast to protonation,[1] which has been shown to be reversible and to occur predominantly at nitrogen to give the thermodynamically more stable dithiolium cations (14).

Treatment of the iodides (6a)—(9a) with aqueous or ethanolic methylamine gave the symmetrical 6a-thia-1,6-diazapentalenes (15)—(18), respectively. Minor products were formed concomitantly. Compounds (17) and (18) were accompanied by small amounts of the red thiones (19) (2·5%) and (20) (11%). The thiones result from reductive cleavage of the S–N bond in the isothiazolium salts (8a) and (9a) by methanethiolate ion liberated in the main reaction.[4] A small quantity (1%) of the 1,6a-dithia-6-azapentalene (2) was also formed with the 6a-thia-1,6-diazapentalene (15), and a substantial quantity (10%) of the trimethyl derivative (3) was produced with the main product (16). If *N*-methylation had accompanied *S*-methylation to a small extent the products from the 1,6a-dithia-6-azapentalenes (2) and (3) would have contained small quantities of the Vilsmeier salts (10) and (11), which, when treated with methylamine, would have produced[1,2] the side products (2) and (3). However, the ^{1}H n.m.r. spectra of concentrated solutions of the crude methylation products from compounds (2) and (3) showed

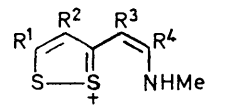
[1] Part XIV, J. G. Dingwall, A. S. Ingram, D. H. Reid, and J. D. Symon, *J.C.S. Perkin I*, 1973, 2351.
[2] Preliminary communication, D. H. Reid and J. D. Symon, *Chem. Comm.*, 1969, 1314.
[3] D. H. Reid, *J. Chem. Soc.* (*C*), 1971, 3187.
[4] R. M. Christie, A. R. Dunn, A. S. Ingram, and D. H. Reid, unpublished data.

only the signals of the iodides (6a) and (7a). The minor products (2) and (3) result therefore from *S*-demethylation of the iodides (6a) and (7a) by methylamine. A precedent exists for such behaviour. In an attempt [5] to synthesise the 6a-thia-1,6-diazapentalene (21), the iodide (22) obtained by methylation of the 1,6a-dithia-6-azapentalene (23) underwent *S*-demethylation when boiled with aniline in acetic acid, regenerating compound (23).

The ^{1}H n.m.r. spectra of the 6a-thia-1,6-diazapentalenes (15)—(18) in $CDCl_3$ (Table) show magnetic equivalence of ring protons or substituents at the pairs of sites N-1 and N-6, C-2 and C-5, and C-3 and C-4, thereby demonstrating that these compounds *in solution* possess real or time-averaged C_{2v} symmetry. The derivative (16) was studied in more detail. Its spectra in $CDCl_3$, CS_2, and $(CD_3)_2SO$ were identical in pattern, and consisted of only three sharp signals (3 : 3 : 1 intensities). These



	R^1	R^2	R^3	R^4	X
(10)	H	H	H	H	I
(11)	H	Me	Me	H	I
(12)	H	Me	Me	H	ClO_4
(13)	H	$[CH_2]_3$		H	ClO_4



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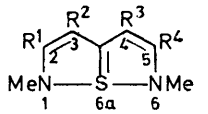
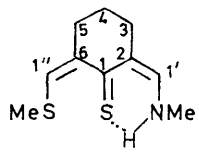


	R^1	R^2	R^3	R^4
(15)	H	H	H	H
(16)	H	Me	Me	H
(17)	H	$[CH_2]_3$		H
(18)	Me	H	H	Me



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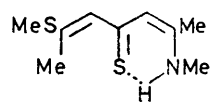
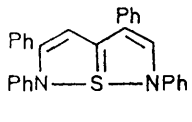


(20)

results exclude a ' frozen ' monocyclic isothiazole structure (24). The pattern of the spectrum in CS_2 also remained unchanged down to −70 °C, below which decreasing solubility prevented further study. In addition to compounds (15)—(18), members of eight other heterocyclic systems of the 6a-thiathiophthen type are now known in which identical groups or ring heteroatoms



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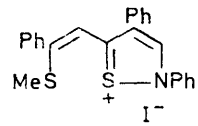

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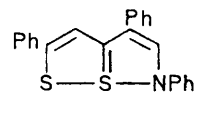

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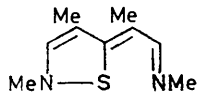

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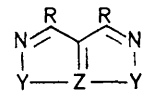
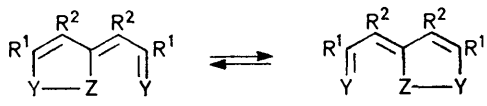


(25) Y = O, Z = S
(26) Y = O, Z = Se
(27) Y = O Z = Te
(28) Y = ArN, Z = Se



(29a) (29b)

(30a) (30b)

occupy the pairs of sites 1 and 6, 2 and 5, and 3 and 4. These systems are the 6a-thiathiophthens (1; Y = Z = S),[6-8] 6a-selenathiophthens (1; Y = S, Z = Se),[3]

Chemical shifts (δ) [a] and chemical shift differences (Δδ) in the ^{1}H n.m.r. spectra of the 6a-thia-1,6-diazapentalenes (15)—(18) and the corresponding 1,6a-dithia-6-azapentalenes (2)—(5) (solutions in $CDCl_3$; *J* in Hz)

	Proton signals (δ)					
	R^3 [b]	Δδ	R^4 [c]	Δδ	NMe	Δδ
(15)	6·37d $J_{3,2}$ 3·8	0·68	7·71dq $J_{2,3}$ 3·8 $J_{2,NMe}$ 0·6	0·20	3·45d $J_{NMe,2}$ 0·6	0·18
(2)	7·05d $J_{4,5}$ 3·4		7·91dq $J_{5,4}$ 3·4 $J_{5,NMe}$ 0·6		3·63 $J_{NMe,5}$ 0·6	
(16)	2·49	0·19	7·48		3·40	0·14
(3)	2·52d $J_{4-Me,5}$ 0·5		7·67m		3·54d	
(17)	1·92quint(4-H_2) 2·74t(3- + 5-H_2)	0·28	7·47		3·44	0·15
(4)	1·92m(4-H_2) 2·76t(5-H_2)		7·75br		3·59d $J_{NMe,6}$ 0·6	
(18)	6·16	0·60	2·13	0·10	3·25	0·11
(5)	6·76		2·23		3·36	

[a] Unless otherwise stated values refer to singlet absorptions. [b] Compounds (15)—(18), $R^2 = R^3$. [c] Compounds (15)—(18), $R^1 = R^4$.

[5] E. Klingsberg, *J. Org. Chem.*, 1968, **33**, 2915.
[6] G. Pfister-Guillouzo and N. Lozac'h, *Bull. Soc. chim. France*, 1964, 3254.
[7] C. Portail and J. Vialle, *Bull. Soc. chim. France*, 1966, 3187.
[8] J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc.* (*C*), 1968, 2543.

6a-selenaselenophthens (1; Y = Z = Se),[9] 1,6-dioxa-6a-thiapentalenes (1; Y = O, Z = S),[10] and the diaza-heterocycles (25),[11] (26),[12,13] (27),[14] and (28).[14] In all cases the ^{1}H n.m.r. spectra of symmetrically substituted derivatives show magnetic equivalence of ring protons or substituents at these pairs of sites. There is at present no evidence for a rapid valence isomerisation (29a) ⇌ (29b) or (30a) ⇌ (30b), and these compounds are all satisfactorily represented by bicyclic structures.

A crystallographic study of the 6a-thia-1,6-diazapentalene (17) has been carried out recently.[15] Although the molecule is not C_{2v}-symmetrical in the solid state, doubtless owing to distortion of the relatively weak three-centre S–N bonds by intermolecular forces in the anisotropic crystal state, the S–N bond lengths (1·901 and 1·948 Å) are both significantly greater than normal covalent S–N bond lengths (*ca.* 1·75 Å). In this aspect of its structure, compound (17) resembles 6a-thiathiophthen,[16] 6a-selenathiophthen,[17] 6a-selenaselenophthen,[18] and compound (26; RR = CH_2·CMe_2·CH_2).[13]

The properties of the 6a-thia-1,6-diazapentalenes (15)—(18) resemble those of enamines and pyrroles. The solids become brown in air, and solutions in polar solvents rapidly deposit brown oils. Decomposition is accelerated by light. The chemical shifts of 3(4)-H in compounds (15) (δ 6·37) and (18) (δ 6·16) indicate marked shielding, and approach the values for protons in electron-rich heteroaromatic compounds (*N*-methylpyrrole:[19] 2-H, δ 6·37; 3-H, δ 5·92). Ring protons and substituents in the 6a-thia-1,6-diazapentalenes (15)—(18) are shielded relative to the equivalent protons or substituents of the isothiazole ring in the corresponding 1,6a-dithia-6-azapentalenes (2)—(5) (see Table). The chemical shift difference is greatest for 4-H [≡ 3-H in compounds (15) and (18)] [δ(4-H)(2) − δ(4-H)(15) = 0·68 p.p.m.]. The 2-H,3-H coupling constant in 1,6-dimethyl-6a-thia-1,6-diazapentalene (15) (3·8 Hz) is appreciably larger than the equivalent 4-H,5-H coupling constant in 6-methyl-1,6a-dithia-6-azapentalene (2) (3·4 Hz), indicating that the C(2)—C(3) bond order in 6a-thia-1,6-diazapentalenes is greater than the C(4)—C(5) bond order in the corresponding 1,6a-dithia-6-azapentalenes. The fact that the 2,3- and 4,5-bonds (1·367 and 1·358 Å) in compound (17)[15] are appreciably shorter than the equivalent 4,5-bond (1·388 Å) in compound (23)[20] confirms this conclusion.

The electron-rich nature of the 6a-thia-1,6-diazapentalenes (15)—(18) deduced from ^{1}H n.m.r. chemical shift data is evidenced chemically by the formation of stable black 1 : 1 charge-transfer complexes with 1,3,5-trinitrobenzene. The spectra of the complexes show an upfield shift of all proton signals relative to those of the uncomplexed component molecules in the complexes.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were measured with a Unicam SP 800 spectrophotometer. Light absorption data refer to solutions in cyclohexane, unless otherwise stated. ^{1}H N.m.r. spectra were determined at 100 MHz (indicated) with a Varian HA100 spectrometer or at 60 MHz with a Perkin-Elmer R10 spectrometer. Solutions were 0·4—0·6M, tetramethylsilane was used as internal reference, and *J* values were measured on the 100 Hz scale. Unless otherwise stated values refer to singlet absorptions. Multiplicities refer to the appearance of signals on the 100 Hz scale. Mass spectra were obtained with an A.E.I. MS902 spectrometer. Column chromatography was carried out with Spence grade H alumina. Solvent mixtures are described in ratios of volumes. Solutions were dried over sodium sulphate and evaporated at reduced pressure.

Materials.—Perchloric acid refers to 70—72% (w/w) perchloric acid. Aqueous methylamine was 25—30% (w/v) and ethanolic methylamine was 33% (w/w). Light petroleum was of boiling range 40—60°.

S-*Methylation of* 6-*Methyl*-1,6a-*dithia*-6-*azapentalenes: Preparation of* 2-*Methyl*-5-(2-*methylthiovinyl*)*isothiazolium Salts.*—The following general procedure was used (deviations are given in individual cases). Methyl iodide (6·2 ml, 100 mmol) was added to a solution of the 6-methyl-1,6a-dithia-6-azapentalene (10 mmol) in acetonitrile (25 ml) and the solution was heated at 65° for 15 min. Addition of ether to the cooled mixture gave the iodide, which was recrystallised from ethanol. Perchloric acid (0·33 ml, 4 mmol) was added to a suspension of the iodide (2 mmol) in acetonitrile (5 ml). After 10 min ether was added to the resulting solution. The precipitated perchlorate was recrystallised from ethanol.

2-*Methyl*-5-(2-*methylthiovinyl*)*isothiazolium iodide* (6a) *and perchlorate* (6b) *from* 6-*methyl*-1,6a-*dithia*-6-*azapentalene* (2). The *iodide* (6a) (2·95 g, 99%) was obtained as yellow prisms, m.p. 143—145° (decomp.) (Found: C, 28·3; H, 3·6; N, 4·6. $C_7H_{10}INS_2$ requires C, 28·1; H, 3·4; N, 4·7%); δ [$(CD_3)_2SO$] 2·84 (3H, SMe), 4·34 (3H, NMe), 7·32 (1H, d, $J_{1',2'}$ 9·6 Hz, 1'-H), 7·79 (1H, d, $J_{2',1'}$ 9·6 Hz, 2'-H), 7·80 (1H, d, $J_{4,3}$ 2·7 Hz, 4-H), and 9·29 (1H, d, $J_{3,4}$ 2·7 Hz, 3-H). The *perchlorate* (6b) (96%) formed pale yellow needles, m.p. 95° (decomp.) (Found: C, 30·8; H, 3·9; N, 4·9. $C_7H_{10}ClNO_4S_2$ requires C, 30·9; H, 3·7; N, 5·2%); $\lambda_{max.}$ [MeOH–2% (v/v) $HClO_4$] 372 (log ε 4·20), 273infl (3·64), 234 (3·89), and 210sh nm (3·77); δ [$(CD_3)_2SO$] 2·79 (3H, SMe), 4·25 (3H, NMe), 7·23 (1H, d, $J_{1',2'}$ 9·7 Hz, 1'-H), 7·68 (1H, d, $J_{2',1'}$ 9·7 Hz, 2'-H), 7·68 (1H, d, $J_{4,3}$ 2·9 Hz, 4-H), and 9·11 (1H, d, $J_{3,4}$ 2·9 Hz, 3-H); δ (CF_3·CO_2H) 2·79 (3H, SMe), 4·31 (3H, NMe), 7·10 (1H, d, $J_{1',2'}$ 9·7 Hz, 1'-H), 7·45 (1H, d, $J_{4,3}$ 2·8 Hz, 4H), 7·49 (1H, d, $J_{2',1'}$ 9·7 Hz, 2'-H), and 8·69 (1H, d, $J_{3,4}$ 2·8 Hz, 3-H).

[9] M. G. Jackson and D. H. Reid, unpublished data.
[10] D. H. Reid and R. G. Webster, *J.C.S. Chem. Comm.*, 1972, 1283.
[11] R. J. S. Beer and A. J. Poole, *Tetrahedron Letters*, 1972, 1835.
[12] D. Pacquer, M. Perrier, and J. Vialle, *Bull. Soc. chim. France*, 1970, 4517.
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[16] L. K. Hansen and A. Hordvik, *Acta Chem. Scand.*, 1970, **24**, 2246; *ibid.*, 1973, **27**, 411.
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[18] A. Hordvik and K. Julshamn, *Acta Chem. Scand.*, 1971, **25**, 2507.
[19] R. L. Hinman and S. Theodoropulos, *J. Org. Chem.*, 1963, **28**, 3052.
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2,4-*Dimethyl*-5-(1-*methyl*-2-*methylthiovinyl*)*isothiazolium iodide* (7a) *and perchlorate* (7b) *from* 3,4,6-*trimethyl*-1,6a-*dithia*-6-*azapentalene* (3). Methylation in acetonitrile (40 ml) gave the *iodide* (7a) (3·17 g, 98%). Recrystallisation from acetonitrile gave yellow needles, m.p. 175—177° (decomp.) (Found: C, 33·1; H, 4·5; N, 4·2. $C_9H_{14}INS_2$ requires C, 33·0; H, 4·3; N, 4·3%); δ [$(CD_3)_2SO$] 2·22 (3H, d, $J_{1'\text{-Me},2'}$ 1·2 Hz, 1'-Me), 2·32 (3H, 4-Me), 2·48 (3H, SMe), 4·25 (3H, NMe), 6·99br (1H, 2'-H), and 9·20 (1H, 3-H). The *perchlorate* (7b) (83%) formed yellow needles, m.p. 115—120° (Found: C, 35·9; H, 4·9; N, 4·9. $C_9H_{14}ClNO_4S_2$ requires C, 36·0; H, 4·7; N, 4·7%); $\lambda_{max.}$ (MeOH) 377 (log ε 4·20), 270infl (3·74), 246br (3·85), and 209sh nm (3·69); $\lambda_{max.}$ [MeOH–2% (v/v) $HClO_4$] 373 (log ε 4·21), 270infl (3·71), 245br (3·84), and 209sh nm (3·61); δ [$(CD_3)_2SO$] 2·10 (3H, 1'-Me), 2·39 (3H, 4-Me), 2·56 (3H, SMe), 4·16 (3H, NMe), 7·21 (1H, 2'-H), and 8·96 (1H, 3-H); δ ($CF_3{\cdot}CO_2H$) 2·21 (3H, d, $J_{1'\text{-Me},2'}$ 0·9 Hz, 1'-Me), 2·49 (3H, 4-Me), 2·57 (3H, SMe), 4·20 (3H, NMe), 7·67br (1H, 2'-H), and 8·43 (1H, 3-H).

4,5,6,7-*Tetrahydro*-2-*methyl*-7-*methylthiomethylenebenz*[d]-*isothiazolium iodide* (8a) *and perchlorate* (8b) *from* 4,5-*dihydro*-7-*methyl*-3H-*benzo*[cd]-1,6a-*dithia*-6-*azapentalene* (4). The *iodide* (8a) (3·20 g, 95%) was obtained as yellow prisms, m.p. 176—178° (Found: C, 35·3; H, 4·2; N, 4·2. $C_{10}H_{14}INS_2$ requires C, 35·4; H, 4·2; N, 4·1%); δ [$(CD_3)_2SO$] 1·65—2·02 (2H, m, 5-H_2), 2·70 (3H, SMe), 2·80 (2H, t, 6-H_2), 2·90 (2H, t, 4-H_2), 4·24 (3H, NMe), 7·30 (1H, 7-C*H*SMe), and 9·21 (1H, 3-H); δ ($CF_3{\cdot}CO_2H$) 1·85—2·22 (2H, m, 5-H_2), 2·62 (3H, SMe), 2·89 (2H, t, 6-H_2), 2·98 (2H, t, 4-H_2), 4·27 (3H, NMe), 7·02 (1H, 7-C*H*SMe), and 8·67 (1H, 3-H). The *perchlorate* (8b) (98%) formed yellow prisms, m.p. 194—197° (Found: C, 38·2; H, 4·6; N, 4·4. $C_{10}H_{14}ClNO_4S_2$ requires C, 38·5; H, 4·5; N, 4·5%); $\lambda_{max.}$ [MeOH– 2% (v/v) $HClO_4$] 386 (log ε 3·98), 288br (3·62), 240infl (3·83), and 214 nm (3·98); δ [$(CD_3)_2SO$] 1·65—2·05 (2H, m, 5-H_2), 2·66 (3H, SMe), 2·77 (2H, t, 6-H_2), 2·87 (2H, t, 4-H_2), 4·21 (3H, NMe), 7·23 (1H, 7-C*H*SMe), and 9·09 (1H, 3-H); δ ($CF_3{\cdot}CO_2H$) 1·85—2·02 (2H, m, 5-H_2), 2·61 (3H, SMe), 2·88 (2H, t, 6-H_2), 2·97 (2H, t, 4-H_2), 4·22 (3H, NMe), 6·97 (1H, 7-C*H*SMe), and 8·57 (1H, 3-H).

2,3-*Dimethyl*-5-(2-*methyl*-2-*methylthiovinyl*)*isothiazolium iodide* (9a) *and perchlorate* (9b) *from* 2,5,6-*trimethyl*-1,6a-*dithia*-6-*azapentalene* (5). The *iodide* (9a) was obtained from acetonitrile (30 ml) as yellow needles (3·23 g, 99%), m.p. 171—172° (Found: C, 33·1; H, 4·6; N, 4·0. $C_9H_{14}INS_2$ requires C, 33·0; H, 4·3; N, 4·3%); $\lambda_{max.}$ (MeOH) 368 (log ε 4·08), 279br (3·86), 220 (4·31), and 207sh nm (4·22); δ [$(CD_3)_2SO$; 100 MHz] 2·39 (3H, d, $J_{2'\text{-Me},1'}$ 1·2 Hz, 2'-Me), 2·61 (3H, SMe), 2·65 (3H, 3-Me), 4·02 (3H, NMe), 7·20 (1H, q, $J_{1',2'\text{-Me}}$ 1·2 Hz, 1'-H), and 7·51 (1H, 4-H). Perchloric acid (0·33 ml, 4 mmol) was added to a suspension of the iodide (9a) (654 mg, 2 mmol) in acetonitrile (5 ml). Addition of ether to the resulting solution after 10 min precipitated an oil. The ether layer was decanted and the oil was redissolved in acetonitrile (5 ml). Addition of perchloric acid (0·1 ml) followed by ether precipitated a sticky solid which was redissolved in hot ethanol. The cooled solution yielded the *perchlorate* (9b) (263 mg, 44%) as pale yellow needles, m.p. 119—120° (Found: C, 36·2; H, 4·9; N, 5·0. $C_9H_{14}ClNO_4S_2$ requires C, 36·0; H, 4·7; N, 4·7%).

1,6-*Dimethyl*-6a-*thia*-1,6-*diazapentalenes*.— Charge-transfer complexes of 1,6-dimethyl-6a-thia-1,6-diazapentalenes with 1,3,5-trinitrobenzene were prepared from the base (1 mmol) and 1,3,5-trinitrobenzene (1 mmol) in boiling ethanol (10 ml, unless otherwise stated). ^1H N.m.r. spectra of the complexes were obtained with solutions in $CDCl_3$ [0·25M or saturated (<0·25M)].

1,6-*Dimethyl*-6a-*thia*-1,6-*diazapentalene* (15). Aqueous methylamine (50 ml) was added to a solution of the iodide (6a) (2·99 g, 10 mmol) in acetonitrile (100 ml) at room temperature. After 5 min water (500 ml) was added gradually to the red solution, and the resulting mixture was cooled in ice for 30 min. Filtration gave a grey solid and an orange filtrate. The dried solid was extracted with hot cyclohexane (100 ml) and the extract was evaporated. The yellow residue was extracted with boiling light petroleum. Concentration of the extract afforded 1,6-*dimethyl*-6a-*thia*-1,6-*diazapentalene* (471 mg, 31%) which was recrystallised with difficulty from hexane to give yellow plates, m.p. 82—84° (Found: C, 54·6; H, 6·8; N, 18·2. $C_7H_{10}N_2S$ requires C, 54·5; H, 6·5; N, 18·2%); M^+ 154 (100%); $\lambda_{max.}$ 384 (log ε 4·18), 280sh (3·35), 272br (3·44), 226 (4·03), and 205sh nm (3·75). The *trinitrobenzene complex* formed black needles (78%) from ethanol (15 ml), m.p. 129—130° (decomp.) (Found: C, 42·7; H, 3·5; N, 19·2. $C_{13}H_{13}N_5O_6S$ requires C, 42·5; H, 3·6; N, 19·1%); δ 3·40 (6H, 1- + 6-Me), 6·23 [2H, d, $J_{3,2(4,5)}$ 3·8 Hz, 3- + 4-H], 7·63 [2H, d, $J_{2,3(5,4)}$ 3·8 Hz, 2- + 5-H], and 9·23 (3H, trinitrobenzene protons). The orange aqueous filtrate was extracted with ether and the extracts were washed with water, dried and evaporated. Chromatography (alumina, 18 × 2·0 cm) of the residual oil with benzene gave yellow eluates from which 6-methyl-1,6a-dithia-6-azapentalene (2) (15 mg, 1%) was isolated.

1,3,4,6-*Tetramethyl*-6a-*thia*-1,6-*diazapentalene* (16). Aqueous methylamine (100 ml) was added to a stirred suspension of the iodide (7a) (6·54 g, 20 mmol) in ethanol (100 ml) at room temperature. The salt dissolved and yellow crystals appeared. After 2 h water (200 ml) was added and after a further 15 min the mixture was filtered. Recrystallisation of the washed and dried solid (1·82 g, 50%) from acetonitrile gave 1,3,4,6-*tetramethyl*-6a-*thia*-1,6-*diazapentalene* as lemon-yellow needles, m.p. 133—135° (Found: C, 59·4; H, 8·1; N, 15·5; S, 17·7. $C_9H_{14}N_2S$ requires C, 59·3; H, 7·7; N, 15·5; S, 17·6%); M^+ 182 (100%); $\lambda_{max.}$ 402 (log ε 4·23), 285br (3·54), 233 (4·05), and 204 nm (3·91); δ (CS_2) 2·44 (6H, 3- + 4-Me), 3·36 (6H, 1- + 6-Me), and 7·31 (2H, 2- + 5-H); δ [$(CD_3)_2SO$] 2·42 (6H, 3- + 4-Me), 3·32 (6H, 1- + 6-Me), and 7·56 (2H, 2- + 5-H). The *trinitrobenzene complex* formed black needles (92%), m.p. 153—155° (Found: C, 45·8; H, 4·6; N, 17·8. $C_{15}H_{17}N_5O_6S$ requires C, 45·6; H, 4·3; N, 17·7%); δ 2·32 (6H, 3- + 4-Me), 3·28 (6H, 1- + 6-Me), 7·23 (2H, 2- + 5-H), and 9·00 (3H, trinitrobenzene protons). The aqueous filtrates were extracted with benzene and the extracts were washed, dried, and evaporated. Chromatography (alumina; 15 × 3·7 cm) of the residual oil with benzene gave yellow eluates from which 3,4,6-trimethyl-1,6a-dithia-6-azapentalene (3) (370 mg, 10%) was isolated.

4,5-*Dihydro*-1,7-*dimethyl*-3H-*benzo*[cd]-6a-*thia*-1,6-*diazapentalene* (17). Aqueous methylamine (50 ml) was added to a solution of the iodide (8a) (3·39 g, 10 mmol) in methanol (100 ml) at room temperature. After 30 min water (100 ml) was added gradually, and after a further 15 min the mixture was filtered to give yellow crystals and an orange filtrate. The filtrate was extracted with ether, then kept for 18 h while more yellow solid crystallised. The washed and dried crops of yellow crystals were combined (815 mg, 42%) and recrystallised from methanol. 4,5-*Dihydro*-1,7-*dimethyl*-3H-*benzo*[cd]-6a-*thia*-1,6-*diazapentalene* was obtained as

yellow needles, m.p. 90—91° (Found: C, 62·1; H, 7·4; N, 14·4. $C_{10}H_{14}N_2S$ requires C, 61·8; H, 7·3; N, 14·4%); M^+ 194 (100%); $\lambda_{max.}$ 410 (log ε 4·16), 282br (4·08), 231 (4·09), and 205 nm (3·87). The *trinitrobenzene complex* formed black needles (70%), m.p. 112—113° (decomp.) (Found: C, 47·2; H, 4·2; N, 17·1. $C_{16}H_{17}N_5O_6S$ requires C, 47·2; H, 4·2; N, 17·2%); δ 1·82 (2H, quint, 4-H_2), 2·60 (4H, t, 3- + 5-H_2), 3·34 (6H, 1- + 7-Me), 7·26 (2H, 2- + 6-H), and 9·06 (3H, trinitrobenzene protons). The ethereal extracts were washed with water, dried, and evaporated, and the residual dark oil was chromatographed (alumina; 20 × 2·0 cm) with benzene. Evaporation of the orange eluates gave a solid which afforded 2-*methylaminomethylene*-6-*methylthiomethylenecyclohexanethione* (19) (54 mg, 2·5%) as red needles m.p. 115—118° (decomp.) (from cyclohexane) (Found: C, 56·5; H, 7·3; N, 6·4. $C_{10}H_{15}NS_2$ requires C, 56·3; H, 7·1; N, 6·6%); M^+ 213; $\lambda_{max.}$ 436sh (log ε 4·07), 403 (4·33), and 215 nm (4·09); δ ($CDCl_3$; 100 MHz) 1·68—1·86 (2H, m, 4-H_2), 2·24—2·40 (4H, m, 3- + 5-H_2), 2·47 (3H, SMe), 3·16 (3H, d, $J_{NMe,NH}$ 5·1 Hz, NMe), 7·22 (1H, d, $J_{1'\text{-}H,NH}$ 13·2 Hz, 1′-H), 7·67 (1H, t, $J_{1''\text{-}H,5\text{-}H_2}$ 1·7 Hz, 1″-H), and 13·94br (1H, NH). Addition of D_2O to the $CDCl_3$ solution caused the signal at δ 13·94 to disappear and the doublets at δ 3·16 and 7·22 to collapse to singlets.

1,2,5,6-*Tetramethyl*-6a-*thia*-1,6-*diazapentalene* (18). Ethanolic methylamine (100 ml) was added to a stirred suspension of the iodide (9a) (6·54 g, 20 mmol) in ethanol (200 ml) at room temperature. The mixture was stirred for 30 min, water (500 ml) was added, and stirring was continued for a further 30 min before the precipitated yellow solid was filtered off and dissolved in benzene. The residue from the dried and evaporated solution was chromatographed (alumina; 20 × 3·2 cm). Elution with benzene gave yellow eluates which afforded 1,2,5,6-*tetramethyl*-6a-*thia*-1,6-*diazapentalene* (1·945 g, 53%), yellow plates from cyclohexane, m.p. 155—160° (decomp.) (Found: C, 59·1; H, 8·1; N, 15·5. $C_8H_{14}N_2S$ requires C, 59·3; H, 7·7; N, 15·4%); M^+ 182 (100%); $\lambda_{max.}$ 375 (log ε 4·16), 270br (3·61), and 224 nm (3·99). The *trinitrobenzene complex* formed black needles (76%) from ethanol (15 ml), m.p. 135—137° (decomp.) (Found: C, 45·9; H, 4·6; N, 17·9. $C_{15}H_{17}N_5O_6S$ requires C, 45·6; H, 4·3; N, 17·7%); δ 2·03 (6H, 2- + 5-Me), 3·07 (6H, 1- + 6-Me), 5·77 (2H, 3- + 4-H), and 8·98 (3H, trinitrobenzene protons). Continued elution with benzene–ether (9 : 1) brought through red eluates which yielded 2-*methylamino*-6-*methylthiohepta*-2,5-*diene*-4-*thione* (20) (443 mg, 11%), red plates from benzene, m.p. 180° (decomp.) (Found: C, 53·4; H, 7·8; N, 7·3. $C_9H_{15}NS_2$ requires C, 53·7; H, 7·5; N, 7·0%); M^+ 201; $\lambda_{max.}$ 432sh (log ε 3·96), 411 (4·09), and 217 nm (3·95); δ ($CDCl_3$; 100 MHz) 2·06 (3H, 1-Me), 2·18 (3H, d, $J_{7\text{-}Me,6}$ 1·2 Hz, 7-Me), 2·31 (3H, SMe), 3·03 (3H, d, $J_{NMe,NH}$ 5·3 Hz, NMe), 6·16 (1H, 3-H), 6·53br (1H, 5-H), and 13·62vbr (1H, NH). Addition of D_2O containing a trace of $CF_3{\cdot}CO_2D$ to the $CDCl_3$ solution caused the signals at δ 6·16 and 13·62 to disappear and the doublet at δ 3·03 to collapse to a singlet.

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