Synthesis of 6aλ⁴-Thia-1,2,3,5,6-pentaazapentalenes

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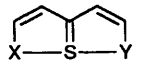
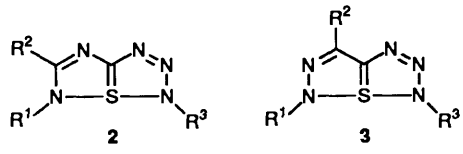
The title compounds have been obtained from 5-amino-1,2,3-thiadiazole **6** by methylation and reaction with arenediazonium tetrafluoroborates; their ^{13}C NMR data and X-ray analysis are discussed in terms of two non-equivalent resonance contributors **11A** and **11B**.

The development of 6aλ⁴-thiapentalenes started in 1958 when Bezzi and co-workers[1] reported the first X-ray crystal structure of such a compound and revealed its unusual bonding properties. In the years following this discovery several theoretical studies appeared[2] and a large diversity of thiapentalenes have been synthesized for X-ray analysis; these include molecules of general type **1** having S–S–S, O–S–O and N–S–N sequences, as well as other combinations of these atoms.[3] Nitrogen atoms have also been introduced into the conjugated framework connecting the X and Y atoms, culminating in the synthesis of 6aλ⁴-thia-1,2,3,4,6-pentaazapentalenes **2**.[4] The 1,2,3,5,6-pentaaza analogues **3** are now described in this paper.†



1
X,Y = O, S, NR

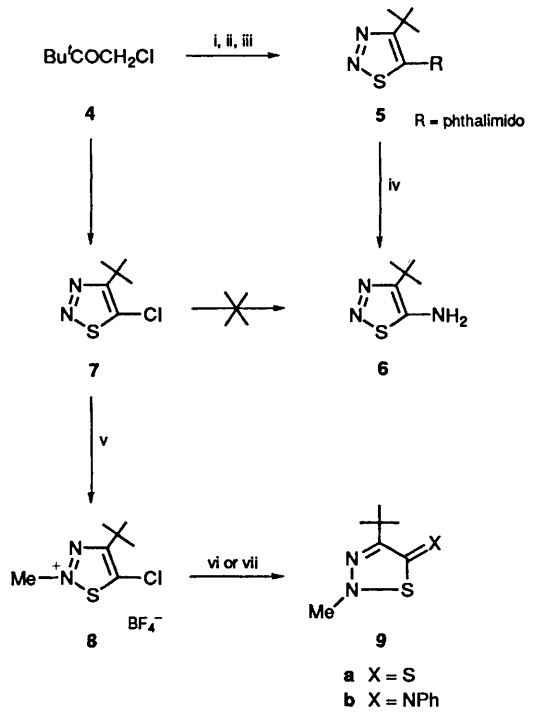


2 **3**

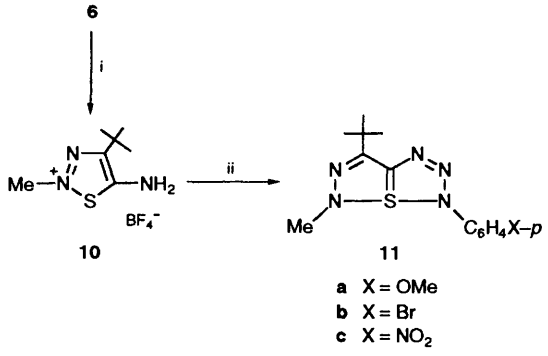
A rational precursor for the title compounds is the 5-aminothiadiazole **6**. We placed a bulky *tert*-butyl group at the 4-position in order to direct methylation exclusively to the N-2 atom in the next step of the reaction sequence; in its absence methylation occurs preferentially at N-3.[5] A convenient method for obtaining compound **6** is shown in Scheme 1 and starts from chloropinacolone **4** which is first converted into the thiadiazole **5** by successive treatment with potassium phthalimide, ethyl carbazate and thionyl chloride (method of Hurd and Mori);[6] the phthalimido group is then removed by hydrazinolysis. The alternative possibility for obtaining the amine **6**, *via* the known[7] 5-chlorothiadiazole **7**, failed since the 5-chloro atom was unreactive towards ammonia. Also, the more reactive methylated derivative **8** could not be transformed into the corresponding amine (or imine) with ammonia in acetonitrile since the thione **9a** (20%, m.p. 112 °C) was obtained. The structure of this unexpected product was unambiguously established by spectral methods and microanalysis, but the mechanism of its formation remains obscure.

With the desired 5-aminothiadiazole **6** to hand, its further conversion into the title thiapentalenes was straightforward and shown in Scheme 2. Thus, treatment of compound **6** with Meerwein's reagent yields the methylated salt **10**, which reacts readily with arenediazonium salts in the presence of pyridine to furnish the yellow thiapentalenes **11a–c**.

These compounds can be described by the dual canonical forms **11A** and **11B**, of which **11A** contributes most to the real



Scheme 1 *Reagents:* i, potassium phthalimide; $EtO_2C–NHNH_2$; iii, $SOCl_2$; iv, N_2H_4; v, $Me_3O^+ BF_4^-$; vi, NH_3; vii, $PhNH_2$



Scheme 2 *Reagents:* i, $Me_3O^+ BF_4^-$; ii, $p\text{-}XC_6H_4N_2^+ BF_4^-$

structure. Indeed, in the ^{13}C NMR spectra (Table 1) the *N*-methyl signals are found at δ ~38, whereas a methylazo group has been reported to resonate at δ 57.[8] Our values are comparable with those of compounds **9a** (δ 42) and **9b** (δ 44); the latter was prepared from the salt **8** and aniline (yield 98%, m.p. 39 °C). The observed shielding by 4–6 ppm reflects the thiapentalenic structure of the molecules for which the three-centre four-electron bonding system is characterized by a high electron density at the terminal heteroatoms, compensated by weakening of the σ-bonds with sulfur.[9] This extra electron

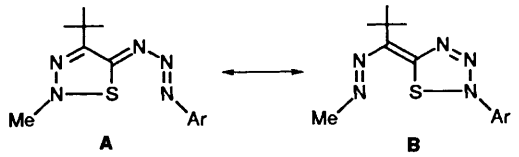
† The numbering used here is that of 1,6,6aλ⁴-trithiapentalene in compliance with common practice.

Table 1 Selected NMR chemical shifts of the thiapentalenes in $CDCl_3$ [a]

Compound	NCH_3	NCH_3 ($^1J_{CH}$)[b]	C-3a	C-4
11a	3.91	37.6 (140)	146.7	151.7
11b	3.95	37.85 (141)	146.6	152.6
11c	4.04	38.3 (141.5)	146.4	154.1

[a] The substituents resonate at the following positions: Bu^t: δ_C 29.1 and 35.5; *p*-$MeOC_6H_4$: δ_C 55.5 (OMe), 137.5 (C_i), 122.1 (C_o), 114.8 (C_m) and 159.2 (C_p); *p*-BrC_6H_4: δ_C 143.6 (C_i), 122.2 (C_o), 132.6 (C_m) and 120.8 (C_p); *p*-$NO_2C_6H_4$: δ_C 149.4 (C_i), 125.3 (C_o), 120.6 (C_m) and 145.8 (C_p). [b] *J* Values are recorded in Hz.

density at N-6 causes a shift of the methyl carbons to higher field compared with those of compounds **9a** and **9b**.



11 Ar = C_6H_4X-*p*

In order to gain more insight into the structural properties of these molecules a single crystal X-ray structure analysis of **11b** was carried out and the results are shown in Fig. 1. The heterobicycle is nearly planar with N(2) deviating most (0.054 Å) from the best plane through the eight atoms. This allows for electron delocalisation of the conjugated system embracing the terminal heteroatoms N(1) and N(6) with bond lengths intermediate between single and double bonds. The atomic sequence N(1)–S(6a)–N(6) makes an angle of 164° and consists of a normal N(6)–S(6a) bond[10] of 1.76 Å and a stretched N(1)–S(6a) bond of 2.06 Å which is considerably shorter than the corresponding van der Waals distance of 3.35 Å. The covalent bond strength can be estimated by using Huggins' eqn. (1),[11] where D_{NS} is the bond dissociation energy

$$D_{NS} = 10^{2(r^*_{NS} - r_{NS})} \quad (1)$$

in kcal mol^{-1}, r_{NS} is the observed bond distance and r^*_{NS} is the computed constant energy distance for N–S (2.58 Å). The calculated dissociation energy for N(1)–S(6a) is 11 kcal mol^{-1} and we conclude that canonical form **11b** is a real, but minor, contributor to the overall structure of the molecule.

Experimental

Typical Procedure: 1-(4-*Bromophenyl*)-4-tert-*butyl*-6-*methyl*-6aλ^4-*thia*-1,2,3,5,6-*pentaazapentalene* **11b**.—A solution of ketone **4** (6.8 g, 0.05 mol) and potassium phthalimide (10 g, 0.05 mol) in dimethylformamide (40 cm^3) was stirred at room temperature for 3 h and then poured into water (100 cm^3). The precipitated *N*-phthalimido-3,3-dimethylbutan-2-one was filtered off, washed with water and dried (13.2 g, 87%), m.p. 101 °C (from EtOH).

A solution of this compound (12.3 g, 0.05 mol), ethoxycarbonylhydrazine (7.8 g, 0.075 mol) and a trace of toluene-*p*-sulfonic acid in toluene (100 cm^3) was refluxed for 16 h with a Dean–Stark water separator. The cooled mixture was then poured into water and the organic phase was collected, washed with water, dried ($MgSO_4$) and evaporated under reduced pressure to give 3,3-dimethyl-1-(*N*-phthalimido)butan-2-one ethoxycarbonylhydrazone as a yellow solid (10.5 g, 34%), m.p. 114 °C.

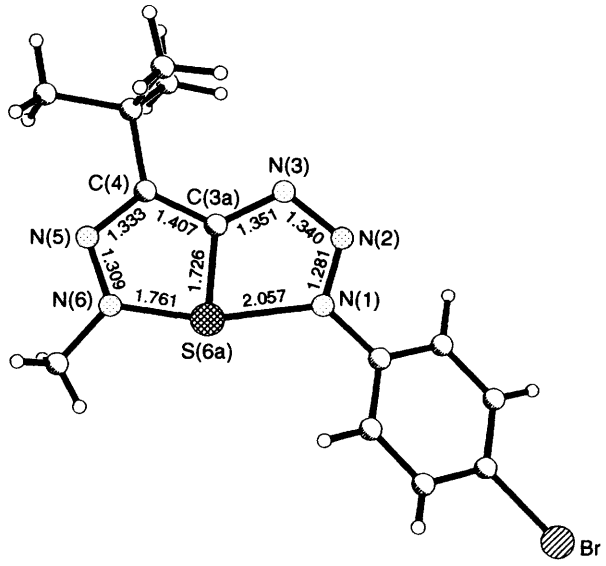


Fig. 1 Molecular structure of **11b** with selected bond lengths (Å)

This compound (16 g, 48 mmol) was added with portions to ice-cooled thionyl chloride (50 cm^3) and the whole was stirred at room temperature for 30 h. The excess of thionyl chloride was distilled off and the residue was chromatographed on silica gel with ethyl acetate–hexane (1:1) as the eluent to give thiadiazole **5** (6.4 g, 47%), m.p. 171 °C.

A solution of 80% hydrazine hydrate (2.3 g) in ethanol (30 cm^3) was added slowly to the thiadiazole **5** (6.4 g, 22 mmol) in boiling ethanol (150 cm^3). After the mixture had cooled, the precipitate was removed and the filtrate was evaporated. The residue was chromatographed on silica gel with diethyl ether–hexane as the eluent to give the 5-aminothiadiazole **6** (2 g, 58%), m.p. 116 °C (from C_6H_6); ν_{max}(KBr)/cm^{-1} 3444s, 3316s, 3190s, 2970s and 1628s; δ_H($CDCl_3$, 400 MHz) 1.48 (9 H, s, Bu^t) and 5.1 (2 H, br, NH_2); δ_C($CDCl_3$) 29.5 and 33.3 (Bu^t), 151.6 (C-4) and 159.2 (C-5).

A solution of the thiadiazole **6** (2 g, 13 mmol) and trimethyloxonium tetrafluoroborate (2 g, 14 mmol) in dry dichloromethane (40 cm^3) was stirred at room temperature for 1 day after which it was evaporated and the residue crystallized from ethanol to give the salt **10** (1.12 g, 32%), m.p. 186–190 °C (Found: C, 32.35; H, 5.3. $C_7H_{14}BF_4N_3S$ requires C, 32.45; H, 5.45%); ν_{max}(KBr)/cm^{-1} 3244s and 3052s (NH_2); δ_H[$(CD_3)_2$SO, 400 MHz] 1.38 (9 H, s, Bu^t), 4.09 (3 H, s, NMe) and 8.80 (2 H, br s, NH_2); δ_C[$(CD_3)_2SO$] 27.6 and 33.1 (Bu^t), 43.0 (NMe), 148.0 (C-4) and 168.6 (C-5).

Pyridine (5 cm^3) was added dropwise to an ice-cooled solution of the salt **10** (470 mg, 1.8 mmol) and *p*-bromobenzenediazonium tetrafluoroborate (460 mg, 1.8 mmol) in dry tetrahydrofuran (20 cm^3) and the whole was stirred overnight at room temperature. The reaction mixture was then poured into chloroform (100 cm^3) and washed with 3 mol dm^{-3} aqueous hydrochloric acid (3 × 100 cm^3) and water (100 cm^3). The organic phase was dried ($MgSO_4$) and evaporated and the residue was chromatographed on silica gel with diethyl ether–hexane (1:3) as the eluent to give the thiapentalene **11b** (340 mg, 53%), m.p. 125 °C (yellow crystals from EtOH) (Found: C, 44.2; H, 4.5. $C_{13}H_{16}BrN_5S$ requires C, 44.07; H, 4.55%); δ_H($CDCl_3$, 400 MHz) 1.66 (9 H, s, Bu^t), 3.95 (3 H, s, NMe) and 7.56 and 7.70 (4 H, 2d, C_6H_4); δ_C($CDCl_3$) see Table 1; *m/z* 355/353 ($M^{\bullet+}$, 3%), 185/183 ($BrC_6H_4N_2^+$, 100), 157/155 ($BrC_6H_4^+$, 60), 76 ($C_6H_4^{\bullet+}$, 19), 75 (15), 61 (10), 57 (Bu^+, 33) and 43 (MeN_2^+, 49).

Note: The thiapentalenes **11a** (23%, m.p. 120 °C) and **11c** (72%, m.p. 221 °C) were similarly prepared from the thiadiazolium salt **10** and *p*-methoxybenzenediazonium tetrafluoro-

borate and *p*-nitrobenzenediazonium tetrafluoroborate, respectively.

Crystal Structure of Compound **11b**.—*Crystal data.* $C_{13}H_{16}BrN_5S$, $M = 354.3$. Triclinic, $a = 8.808(1)$, $b = 9.521(2)$, $c = 10.362(2)$ Å, $\alpha = 96.93(1)$, $\beta = 105.77(1)$, $\gamma = 109.75(1)°$, $V = 765.1(2)$ Å^3 (by least squares refinement on diffractometer angles of 20 automatically centred reflections, $\lambda = 1.541\,78$ Å), space group $P\bar{1}$ (No. 2), $Z = 2$, $D_x = 1.538$ g cm^{-3}. Yellow blocks from ethanol. Crystal dimensions 0.35 × 0.35 × 0.15 mm^3, μ(Cu-Kα) = 4.918 mm^{-1}.

Data collection and processing. Siemens P4-PC diffractometer, ω–2θ mode with ω scan width 0.60 deg, ω-scan speed 2–60 deg min^{-1}, graphite-monochromatized Cu-Kα radiation; 1979 reflections measured ($2.0 \leqslant 2\theta \leqslant 100.9°$, $+h$, k, l), 1576 unique (merging $R = 0.0294$), giving 1488 observed with $F > 4\sigma(F)$. Three check reflections measured every 100 reflections showed no significant decrease in intensity.

Structure analysis and refinement. Direct methods. Full matrix least-squares on F^2 with all non-hydrogen atoms anisotropic, hydrogen atoms with fixed isotropic U 1.2 times U_{eq} of the parent atom. Final R and ωR_2 values are 0.0532 and 0.1443 for observed reflections. Siemens SHELXTL PLUS (PC version)[12] program used for structure solution and drawings. SHELXL-93 program[13] used for structure refinement.

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