

Cyclic Meso-ionic Compounds. Part 18.^{1a} The Synthesis and Spectroscopic Properties of 1,2,3,4-Thiatriazolium-5-aminides and 1,2,3,4-Tetrazolium-5-thiolates^{1b}

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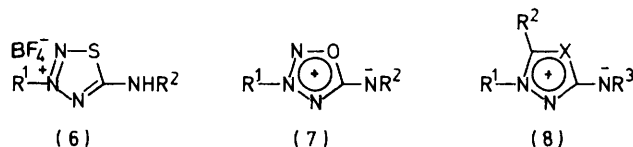
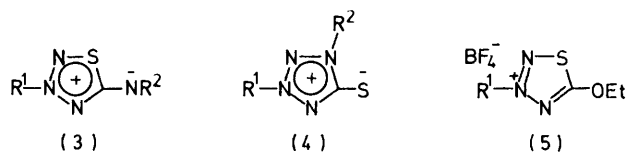
The new meso-ionic systems 1,2,3,4-thiatriazolium-5-aminides (3) and 1,2,3,4-tetrazolium-5-thiolates (4) have been prepared and characterised.

IN the two preceding papers^{1a,2} we have reported the synthesis and characterisation of the pairs of meso-ionic isomers (1a and 2a) and (1b and 2b) and their interconversion (1a, b \rightarrow 2a, b). We now describe



- a; X = O, Y = S
 b; X = O, Y = NR²
 c; X = Y = S

the synthesis of derivatives of another pair of meso-ionic isomers of the general type (1) and (2), namely the 1,2,3,4-thiatriazolium-5-aminides (3) and the 1,2,3,4-tetrazolium-5-thiolates (4) which belong to two new classes of meso-ionic heterocycles.



- a; R¹ = R² = Ph
 b; R¹ = Ph, R² = *p*-MeC₆H₄
 c; R¹ = *p*-MeC₆H₄, R² = Ph
 d; R¹ = R² = *p*-MeC₆H₄
 e; R¹ = Ph, R² = *p*-ClC₆H₄
 f; R¹ = *p*-ClC₆H₄, R² = Ph
 g; R¹ = R² = *p*-ClC₆H₄

The preparation of the tetrafluoroborates (5e—f) has been reported.² When these salts (5e—f) were suspended in benzene and heated under reflux with the appropriate aromatic amine, the arylamino-compounds (6e—f) were obtained in good yield (50—70%).

Attempts to prepare the salt (6g) from compound (5g) and *p*-chloroaniline were unsuccessful. The salts (6e—f) are yellow, crystalline compounds. Their i.r. spectra show absorptions in the regions 3 500—3 600 and 1 560—1 570 cm⁻¹, which can be attributed to the N—H stretching and N—H bending vibrations respectively. An NH signal is observed at low field in their n.m.r. spectra.

Treatment of warm ethanolic solutions of the tetrafluoroborates (6e—f) with sodium hydroxide gave the red, crystalline meso-ionic compounds (3e—f), the i.r. spectra of which show a strong absorption in the region 1 580—1 590 cm⁻¹, which can be assigned to the exocyclic C=N stretching vibration. This is at lower frequency than the corresponding absorption (1 675—1 680 cm⁻¹) of the oxatriazoliumaminides (7). A similar difference in the frequencies of the exocyclic C=N absorptions in the meso-ionic compounds (8; X = S) (1 550—1 580 cm⁻¹)³ and (8; X = O) (1 630—1 670 cm⁻¹)⁴ has been observed.

The u.v. and visible spectra of the thiatriazoliumaminides (3e—f) are very similar to those of the oxatriazoliumaminides (7)¹ [*e.g.* (3a): λ_{max.} 279 and 441 nm (ε 29 300 and 1 830); (7a): λ_{max.} 265 and 410 nm (ε 31 120 and 2 539)]. The n.m.r. spectra of compounds (3e—f) are consistent with the appropriate aryl substituents and their mass spectra⁵ all show intense molecular ions. The dipole moment of compound (3a) in benzene solution has been found to be 3.7 D.⁶

In their physical properties, the thiatriazoliumaminides (3) closely resemble the oxatriazoliumaminides (7).¹ Compounds (7) have been shown to rearrange in ethanolic alkali solution giving the tetrazoliumolates (9).^{1,7} Because of the similarity of the meso-ionic types (3) and (7), compounds (3) might be expected to undergo a similar transformation to give the meso-ionic tetrazoliumthiolates (4), whose synthesis has not been reported. However, all attempts to bring about the rearrangement (3 \rightarrow 4) have been unrewarding, but we have been successful in finding an alternative route to the meso-ionic tetrazoliumthiolates (4). When the tetrafluoroborates (10)¹ and sodium sulphide in dimethylformamide were heated under reflux, a yellow solution was obtained which yielded compounds (4).

The physical properties of the tetrazoliumthiolates (4) are quite different from those of the isomeric thiatriazoliumaminides (3). The i.r. spectra of compounds

(4a, d—g) show a strong absorption in the region 1 365—1 370 cm^{-1} which can be attributed to the C=S stretching frequency. A C=S absorption band is observed at similar frequencies in the i.r. spectra of the meso-ionic compounds (1a) (ν_{max} 1 365—1 375 cm^{-1}) and (1c) (ν_{max} 1 325—1 355 cm^{-1}).²

The u.v. and visible spectra of compounds (4a, d—g) resemble those of compounds (9),^{1a} although the intensity of the absorptions is weaker [e.g. (4a): λ_{max} 222infr., 270, and 386 nm (ϵ 8 260, 17 620, and 1 475); (9a): λ_{max} 225, 263, and 326 nm (ϵ 35 110, 25 280, and 32 430)]. Their mass spectra all show molecular ions.⁵ The dipole moments of the derivatives (4a; 6.5 D), (4e; 6.5 D), and (4f; 5.6 D) have been measured in benzene solution. An analysis of the dipole moments strongly supports the meso-ionic formulation (4).⁶

EXPERIMENTAL

General experimental details are given in Part 8.⁴

3-Aryl-5-arylamino-1,2,3,4-thiazotriazolium Tetrafluoroborates (4).—Aniline (0.9 g), 5-ethoxy-3-phenyl-1,2,3,4-thiazotriazolium tetrafluoroborate (5a) (1.4 g),² and benzene (40 ml) were heated under reflux (15 min). After cooling, light petroleum (b.p. 60—80°) was added. The yellow precipitate was recrystallised from acetone—light petroleum (b.p. 40—60°) and identified as 5-anilino-3-phenyl-1,2,3,4-thiazotriazolium tetrafluoroborate (6a) (1.2 g, 74%), yellow needles, m.p. 174° (Found: C, 45.7; H, 3.5; N, 16.5. $\text{C}_{13}\text{H}_{11}\text{BF}_4\text{N}_4\text{S}$ requires C, 45.6; H, 3.2; N, 16.4%); λ_{max} 240infr., 278, and 390 nm (ϵ 10 970, 21 906, and 2 405); ν_{max} (KBr) 1 020—1 120br., 1 560, 1 620, and 3 600 cm^{-1} ; $\tau[(\text{CD}_3)_2\text{CO}]$ 1.5—2.7 (m, 10 ArH) and 4.7 (br s, NH); m/e 254 ($M^+ - \text{HBF}_4$).

The following compounds were similarly prepared: 3-phenyl-5-p-tolylamino-1,2,3,4-thiazotriazolium tetrafluoroborate (6b) (1.2 g, 69%), orange prisms, m.p. 179° (Found: C, 47.4; H, 3.8; N, 16.0. $\text{C}_{14}\text{H}_{13}\text{BF}_4\text{N}_4\text{S}$ requires C, 47.2; H, 3.65; N, 15.7%); λ_{max} 239infr., 280, and 403 nm (ϵ 10 700, 23 500, and 2 540); ν_{max} (KBr) 1 020—1 100br, 1 560, 1 610, and 3 600 cm^{-1} ; $\tau[(\text{CD}_3)_2\text{CO}]$ 1.5—2.7 (m, ArH), 3.7 (br s, NH), and 7.63 (s, Me); m/e 268 ($M^+ - \text{HBF}_4$); 5-anilino-3-p-tolyl-1,2,3,4-thiazotriazolium tetrafluoroborate (6c) (1.0 g, 58%), yellow needles, m.p. 193° (Found: C, 47.1; H, 3.9; N, 15.9. $\text{C}_{14}\text{H}_{13}\text{BF}_4\text{N}_4\text{S}$ requires C, 47.2; H, 3.65; N, 15.7%); λ_{max} 247sh, 267, 313, and 384infr. nm (ϵ 11 120, 14 220, 14 150, and 2 320); ν_{max} (KBr) 1 040—1 120br, 1 570, 1 610, and 3 600 cm^{-1} ; $\tau[(\text{CD}_3)_2\text{CO}]$ 1.6—2.6 (m, 9 ArH), 3.89br s, (NH), and 7.49 (s, Me); m/e 268 ($M^+ - \text{HBF}_4$); 3-p-tolyl-5-p-tolylamino-1,2,3,4-thiazotriazolium tetrafluoroborate (6d) (1.25 g, 70%), yellow needles, m.p. 195° (Found: C, 48.8; H, 4.2; N, 15.3. $\text{C}_{15}\text{H}_{15}\text{BF}_4\text{N}_4\text{S}$ requires C, 48.7; H, 4.1; N, 15.15%); λ_{max} 247sh, 270, 315, and 398sh nm (ϵ 10 530, 15 200, 13 280, and 1 911); ν_{max} (KBr) 1 060—1 110br, 1 560, 1 620, and 3 600 cm^{-1} ; $\tau[(\text{CD}_3)_2\text{CO}]$ 1.5—2.6 (m, 8 ArH), 3.80 (br s, NH), 7.50 (s, Me), and 7.61 (s, Me); m/e 282 ($M^+ - \text{HBF}_4$); 5-p-chlorophenylamino-3-phenyl-1,2,3,4-thiazotriazolium tetrafluoroborate (6e) (1.0 g, 52%), yellow-orange prisms, m.p. 198° [Found: C, 42.8; H, 2.85; N, 15.0. $\text{C}_{13}\text{H}_{10}\text{BClF}_4\text{N}_4\text{S}$ requires C, 41.5; H, 2.7; N, 14.9%. Found: $M - (\text{HBF}_4)$, 288.022 9. $\text{C}_{13}\text{H}_9\text{ClN}_4\text{S}$ requires $M^{(35)\text{Cl}}$, 288.023 7]; λ_{max} 241infr., 282, and 398sh nm (ϵ 16 260, 41 050, and 3 595); ν_{max} (KBr) 1 020—

1 120br, 1 560, 1 610, and 3 600 cm^{-1} ; $\tau[(\text{CD}_3)_2\text{CO}]$ 1.5—2.5 (m, 9 ArH), and 6.13 (br s, NH); m/e 288 [$M^+ (^{35}\text{Cl}) - (\text{HBF}_4)$]; 5-anilino-3-p-chlorophenyl-1,2,3,4-thiazotriazolium tetrafluoroborate (6f) (1.3 g, 73%), yellow needles, m.p. 202—205° (decomp.) (Found: C, 41.6; H, 2.8; N, 15.0. $\text{C}_{13}\text{H}_{10}\text{BClF}_4\text{N}_4\text{S}$ requires C, 41.5; H, 2.7; N, 14.9%); λ_{max} 247infr., 283br, and 388sh nm (ϵ 12 000, 17 300, and 2 155); ν_{max} (KBr) 1 060—1 120br, 1 570, 1 610, and 3 600 cm^{-1} ; $\tau[(\text{CD}_3)_2\text{CO}]$ 2.45 (s, 9 ArH) and 4.5 (br s, NH); m/e 288 [$M^+ (^{35}\text{Cl}) - (\text{HBF}_4)$].

3-Aryl-1,2,3,4-thiazotriazolium-5-aminides (3).—5-Anilino-3-phenyl-1,2,3,4-thiazotriazolium tetrafluoroborate (6a) (0.6 g) in warm ethanol was treated with 10M sodium hydroxide (1.0 g). The dark red solution was heated on a steam-bath (5—10 min), cooled, and diluted with water (50 ml) giving a red, crystalline precipitate. Recrystallisation from light petroleum (b.p. 60—80°) gave 3-phenyl-1,2,3,4-thiazotriazolium-5-anilide (3a) (0.3 g, 67%) as dark red needles, m.p. 125° (Found: C, 61.2; H, 4.1; N, 22.2%; M^+ , 254. $\text{C}_{13}\text{H}_{10}\text{N}_4\text{S}$ requires C, 61.35; H, 3.9; N, 22.0%; M , 254); λ_{max} 279 and 411 nm (ϵ 29 300 and 1 830); ν_{max} 1 580 and 1 610 cm^{-1} ; τ 1.6—3.0 (m, ArH).

The following compounds were similarly prepared: 3-phenyl-1,2,3,4-thiazotriazolium-5-p-toluidide (3b) (0.3 g, 67%), red plates, m.p. 122° (Found: C, 62.4; H, 4.6; N, 21.1%; M^+ , 268. $\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}$ requires C, 62.7; H, 4.5; N, 20.9%; M , 268); λ_{max} 281 and 450 nm (ϵ 26 800 and 1 950); ν_{max} 1 590 and 1 615 cm^{-1} ; τ 1.7—3.1 (m, 9 ArH) and 7.66 (s, Me); 3-p-tolyl-1,2,3,4-thiazotriazolium-5-anilide (3c) (0.2 g, 40%), dark red needles, m.p. 123° (Found: M , 268.078 9. $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$ requires M , 268.078 3); λ_{max} 237, 290, and 440 nm (ϵ 11 400, 29 050, and 2 250); ν_{max} 1 580 and 1 610 cm^{-1} ; τ 1.8—3.0 (m, 9 ArH) and 7.55 (s, Me); 3-p-tolyl-1,2,3,4-thiazotriazolium-5-p-toluidide (3d) (0.3 g, 66%), red plates, m.p. 162° (Found: M , 282.094 1. $\text{C}_{15}\text{H}_{14}\text{N}_4\text{S}$ requires M , 282.093 9); λ_{max} 235infr., 289, and 448 nm (ϵ 10 150, 25 300, and 1 800); ν_{max} 1 585 and 1 610 cm^{-1} ; τ 1.8—3.1 (m, ArH); 3-phenyl-1,2,3,4-thiazotriazolium-5-p-chloroanilide (3e) (0.36 g, 65%), dark red needles, m.p. 136° [Found: C, 54.1; H, 3.4; N, 19.2%; $M^+ (^{35}\text{Cl})$, 288. $\text{C}_{13}\text{H}_9\text{ClN}_4\text{S}$ requires C, 54.05; H, 3.1; N, 19.9%; $M^{(35)\text{Cl}}$, 288]; λ_{max} 284 and 442 nm (ϵ 25 400 and 1 805); ν_{max} 1 580 and 1 610 cm^{-1} ; τ 1.7—3.2 (m, ArH); 3-p-chlorophenyl-1,2,3,4-thiazotriazolium-5-anilide (3f) (0.33 g, 65%), dark red plates, m.p. 121° (Found: M , 288.024 2. $\text{C}_{13}\text{H}_9\text{ClN}_4\text{S}$ requires M , 288.023 7); λ_{max} 235infr., 285, and 448 nm (ϵ 16 150, 44 800, and 2 250); ν_{max} 1 580 and 1 610 cm^{-1} ; τ 1.7—3.0 (m, ArH).

1,3-Diaryl-1,2,3,4-tetrazolium-5-thiolates (4).—Finely powdered sodium sulphide (0.3 g) was added to 5-ethoxy-1,3-diphenyl-1,2,3,4-tetrazolium tetrafluoroborate (10a) (0.4 g) in dimethylformamide (15 ml) and the mixture was heated to boiling point and then immediately cooled. The resulting yellow solution was diluted with water (50 ml) and an intense yellow precipitate gradually formed. The precipitate was washed with water, dried, purified by t.l.c. (silica gel—chloroform) recrystallised from aqueous methanol, and identified as 1,3-diphenyl-1,2,3,4-tetrazolium-5-thiolate (4a) (0.2 g, 66%), lemon-yellow needles, m.p. 155° (lit.,⁹ 153°) (Found: C, 61.2; H, 4.1; N, 22.0%; M^+ 254. Calc. for $\text{C}_{13}\text{H}_{10}\text{N}_4\text{S}$: C, 61.35; H, 3.9; N, 22.0%; M , 254); λ_{max} 222infr., 270, and 386 nm (ϵ 8 260, 17 620, and 1 475); ν_{max} 1 370 cm^{-1} ; τ 1.8—2.5 (m, ArH).

The following compounds were similarly prepared: 1,3-di-p-tolyl-1,2,3,4-tetrazolium-5-thiolate (4d) (0.13 g, 45%),

yellow needles, m.p. 192° (Found: C, 64.0; H, 5.2; N, 20.0%; M^+ , 282. $C_{15}H_{14}N_4S$ requires C, 63.8; H, 5.0; N, 19.8%; M , 282); λ_{\max} . 220, 273, and 382 nm (ϵ 22 250, 32 190, and 3 045); ν_{\max} . 1 370 cm^{-1} ; τ 1.96 and 2.62 (A_2B_2 , J_{AB} 9 Hz, p -MeC₆H₄), 2.05 and 2.62 ($A_2'B_2'$, $J_{A'B'}$ 9 Hz, p -MeC₆H₄), and 7.55 (s, 2 × Me); 1-*p*-chlorophenyl-3-phenyl-1,2,3,4-tetrazolium-5-thiolate (4e) (0.14 g, 42%), yellow needles, m.p. 178° [Found: C, 54.2; H, 3.4; N, 19.4%; $M^{+}(^{35}Cl)$, 288. $C_{13}H_9ClN_4S$ requires C, 54.05; H, 3.1; N, 19.4; $M(^{35}Cl)$, 288]; λ_{\max} . 216, 272, and 389 nm (ϵ 16 750, 24 850, and 2 875); ν_{\max} . 1 370 cm^{-1} ; τ 1.7—2.5 (m, ArH); 3-*p*-chlorophenyl-1-phenyl-1,2,3,4-tetrazolium-5-thiolate (4f) (0.11 g, 35%), yellow needles, m.p. 189° [Found: C, 53.85; H, 3.4; N, 19.3%; $M^{+}(^{35}Cl)$, 288]; λ_{\max} . 218, 274, and 388 nm (ϵ 13 180, 29 050, and 2 340); ν_{\max} . 1 370 cm^{-1} ; τ 1.8—2.5 (m, ArH); 1,3-di-*p*-chlorophenyl-1,2,3,4-tetrazolium-5-thiolate (4g) (0.16 g, 43%), yellow needles, m.p. 230° [Found: C, 48.3; H, 2.8; N, 17.5%; $M^{+}(^{35}Cl)$, 322. $C_{13}H_8Cl_2N_4S$ requires C, 48.3; H, 2.5; N, 17.3%; $M(^{35}Cl)$, 322]; λ_{\max} . 217, 276, and 392 nm (ϵ 17 618, 29 650, and 2 695); ν_{\max} . 1 365 cm^{-1} ; τ 1.8 and

2.4 (A_2B_2 , J_{AB} 9 Hz, p -ClC₆H₄), and 1.85 and 2.44 ($A_2'B_2'$, $J_{A'B'}$ 9 Hz, p -ClC₆H₄).

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