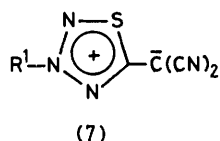
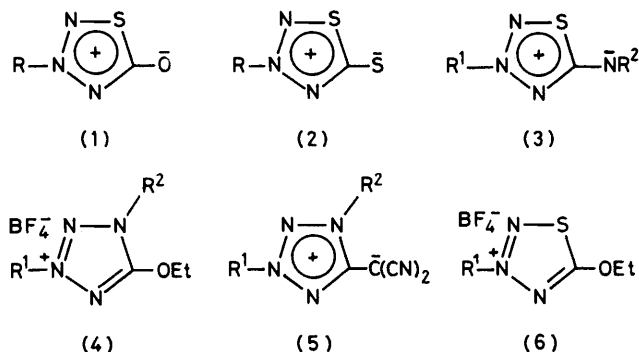


## Cyclic Meso-ionic Compounds. Part 19.<sup>1a</sup> The Reaction of 5-Ethoxy-1,2,3,4-tetrazolium and 5-Ethoxy-1,2,3,4-thiatriazolium Tetrafluoroborates with Nucleophiles. The Preparation of 1,2,3,4-Tetrazolium- and 1,2,3,4-Thiatriazolium-5-dicyanomethylides<sup>1b</sup>

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The reaction of 5-ethoxy-1,2,3,4-tetrazolium (4) and 5-ethoxy-1,2,3,4-thiatriazolium tetrafluoroborates (6) with malononitrile and triethylamine gives the meso-ionic 1,2,3,4-tetrazolium- and 1,2,3,4-thiatriazolium-5-dicyanomethylides (8) and (9) which are new classes of meso-ionic heterocycle. The meso-ionic 1,2,3,4-tetrazoles (8) and (9) form 1,2,3,4-tetrazolium tetrafluoroborates which react with aqueous sodium sulphide giving the formazans (11) and (13).

THE reaction of meso-ionic tetrafluoroborate salts, prepared from the meso-ionic heterocycle and triethyloxonium tetrafluoroborate ( $\text{Et}_3\text{O}^+ \text{BF}_4^-$ ), with nucleophile reagents (e.g.  $\text{Na}_2\text{S}$ ,  $\text{RNH}_2$ ) has been found to be a very useful method for preparing new meso-ionic systems.<sup>2</sup> For example, we have shown previously that



a;  $\text{R}^1 = \text{R}^2 = \text{Ph}$   
 b;  $\text{R}^1 = \text{R}^2 = p\text{-MeC}_6\text{H}_4$   
 c;  $\text{R}^1 = \text{R}^2 = p\text{-ClC}_6\text{H}_4$

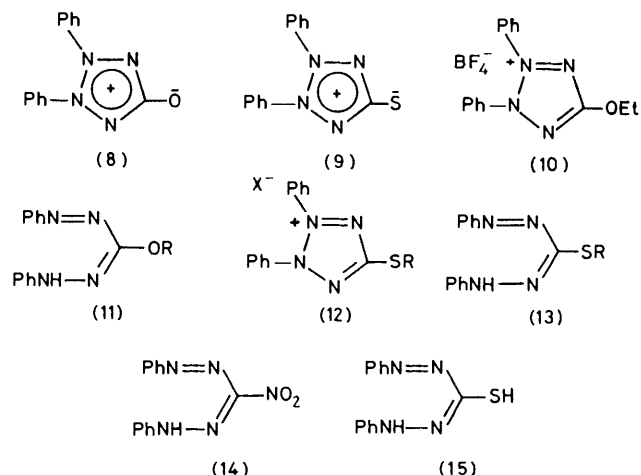
treatment of the tetrafluoroborate salts of the meso-ionic thiatriazoliumolates (1) with sodium sulphide yields the meso-ionic thiatriazoliumthiolates (2).<sup>3</sup> Similarly, treatment with aromatic amines provides a route to the meso-ionic thiatriazolium-5-aminides (3).<sup>1</sup> We now show that this type of procedure can be used to prepare novel meso-ionic heterocycles which are associated with an exocyclic carbanionoid group.

Heating the tetrafluoroborate (4a)<sup>4</sup> with malononitrile and triethylamine in acetonitrile solution gave the yellow, crystalline 1,2,3,4-tetrazolium-5-dicyanomethylide (5a). The derivative (5b) was prepared similarly. The spectral properties of (5a, b) support their formulation as meso-ionic tetrazoles. Their i.r. spectra show absorption bands which can be assigned to the C=C

(1 545  $\text{cm}^{-1}$ ) and  $\text{C}\equiv\text{N}$  (2 200  $\text{cm}^{-1}$ ) stretching frequencies. Their mass spectra show an intense molecular ion. The dipole moment of (5a) has been measured in benzene solution and found to be 9.5 D;<sup>5</sup> this large value strongly supports the meso-ionic formulation (5).

Using identical conditions to those just described, we have treated the tetrafluoroborates (6)<sup>3</sup> with malononitrile and triethylamine and isolated a new class of meso-ionic heterocycle, the 3-aryl-1,2,3,4-thiatriazolium-dicyanomethylides (7a-c), in good yield. The structures (7) are supported by spectral properties. Thus, the i.r. spectra show C=C (1 500  $\text{cm}^{-1}$ ) and  $\text{C}\equiv\text{N}$  (2 200  $\text{cm}^{-1}$ ) stretching vibrations and the mass spectra show strong molecular ions. Compound (7a) has a dipole moment of 8.8 D in benzene solution,<sup>5</sup> and this large value is in good agreement with the meso-ionic structure (7).

The usefulness of tetrafluoroborate salts in preparing new classes of meso-ionic heterocycle has encouraged us to examine the properties of the tetrafluoroborate salts of other meso-ionic systems. In particular, we have examined the meso-ionic tetrazoliumolates (8)<sup>6</sup> and the tetrazoliumthiolates (9).<sup>7-10</sup>



When the diphenyltetrazoliumolate (8)<sup>6</sup> was added to a solution of triethyloxonium tetrafluoroborate ( $\text{Et}_3\text{O}^+ \text{BF}_4^-$ )<sup>11</sup> in dichloromethane, the tetrafluoroborate (10)

was obtained in good yield, the structure of which is supported by its spectral properties. The reactions of (10) with aromatic amines or with malononitrile in the presence of triethylamine were unrewarding. Furthermore, treatment of (10) with aqueous sodium sulphide did not give the expected meso-ionic tetrazolium-thiolate (9), but instead ring opening occurred giving the formazan (11; R = Et) in high yield.

Under similar conditions, the diphenyltetrazolium-thiolate (9) gave the tetrafluoroborate (12; R = Et, X = BF<sub>4</sub>) which on treatment with aqueous sodium sulphide gave the formazan (13; R = Et). Similarly, the tetrazolium iodide (12; R = Me, X = I), prepared from the tetrazoliumthiolate (9) and methyl iodide,<sup>8</sup> gave the formazan (13; R = Me).

#### EXPERIMENTAL

General experimental details are given in Part 8.<sup>12</sup>

**1,3-Diaryl-1,2,3,4-tetrazolium-5-dicyanomethylides (5).**—Triethylamine (0.4 g) was added to a solution of 5-ethoxy-1,3-diphenyl-1,2,3,4-tetrazolium tetrafluoroborate (4a) (1.2 g)<sup>4</sup> and malononitrile (0.4 g) in acetonitrile (25 ml). The mixture was heated under reflux (30 min) and evaporation of the orange solution gave a yellow oil which crystallised from acetone-ether. After recrystallisation from acetone-ether, the product was identified as 1,3-diphenyl-1,2,3,4-tetrazolium-5-dicyanomethylide (5a) (0.5 g, 52%), yellow cubes, m.p. 234° (Found: C, 67.2; H, 3.7; N, 29.2%; M<sup>+</sup>, 286. C<sub>18</sub>H<sub>10</sub>N<sub>6</sub> requires C, 67.1; H, 3.5; N, 29.35%; M, 286); λ<sub>max.</sub> 223(sh), 273, and 394 nm (ε 8 880, 26 850, and 1 358); ν<sub>max.</sub> 1 545 and 2 200 cm<sup>-1</sup>; τ 1.7—2.3 (m, ArH).

**1,3-Di-p-tolyl-1,2,3,4-tetrazolium-5-dicyanomethylide (5b)** was prepared similarly (0.3 g, 27%), and purified by t.l.c. [silica gel; chloroform-ethyl acetate (3:2)], yellow plates, m.p. 222° (Found: C, 68.5; H, 4.7; N, 26.7%; M<sup>+</sup>, 314. C<sub>18</sub>H<sub>14</sub>N<sub>6</sub> requires C, 68.8; H, 4.5; N, 26.7%; M, 314); λ<sub>max.</sub> 221inf., 279, 349inf., and 394(sh) nm (ε 28 900, 35 150, 2 065, and 1 432); ν<sub>max.</sub> 1 545 and 2 200 cm<sup>-1</sup>; τ 1.8—2.6 (m, 8 ArH) and 7.52 (s, 2 × Me).

**3-Aryl-1,2,3,4-thiaziazolium-5-dicyanomethylides (7).**—Triethylamine (0.3 g) was added to a solution of 5-ethoxy-3-phenyl-1,2,3,4-thiaziazolium tetrafluoroborate (6a) (0.6 g)<sup>3</sup> and malononitrile (0.3 g) in acetonitrile (20 ml). The solution was heated under reflux (10 min) and then evaporated giving an oil which by recrystallisation from ethanol gave 3-phenyl-1,2,3,4-thiaziazolium-5-dicyanomethylide (7a) (0.4 g, 87%), orange plates, m.p. 200° (decomp.) (Found: C, 52.6; H, 2.5; N, 30.9%; M<sup>+</sup>, 227. C<sub>10</sub>H<sub>5</sub>N<sub>5</sub>S requires C, 52.85; H, 2.2; N, 30.8%; M, 227); λ<sub>max.</sub> 232inf., 293, and 465 nm (ε 6 170, 37 800, and 4 000); ν<sub>max.</sub> 1 500 and 2 200 cm<sup>-1</sup>; τ 1.5—2.5 (m, ArH).

The following derivatives were similarly prepared: 3-p-tolyl-1,2,3,4-thiaziazolium-5-dicyanomethylide (7b) (0.1 g, 43%), deep orange plates, m.p. 234° (decomp.) (Found: C, 54.5; H, 3.2; N, 29.1%; M<sup>+</sup>, 241. C<sub>11</sub>H<sub>7</sub>N<sub>5</sub>S requires C, 54.75; H, 2.9; N, 29.0%; M, 241); λ<sub>max.</sub> 239, 293, 305(sh), and 461 nm (ε 5 470, 25 400, 24 300, and 3 670); ν<sub>max.</sub> 1 500 and 2 250 cm<sup>-1</sup>; τ 1.83 and 2.58 (A<sub>2</sub>B<sub>2</sub>, J<sub>AB</sub> 9 Hz, *p*-MeC<sub>6</sub>H<sub>4</sub>) and 7.48 (s, Me); 3-*p*-chlorophenyl-1,2,3,4-thiaziazolium-5-dicyanomethylide (7c) (0.17 g, 63%), deep orange plates, m.p. 220° (decomp.) [Found: C, 45.6; H, 1.8; N, 26.9%; M<sup>+</sup>(<sup>35</sup>Cl), 261. C<sub>10</sub>H<sub>4</sub>ClN<sub>5</sub>S requires C, 45.9; H, 1.5; N, 26.8%; M(<sup>35</sup>Cl), 261]; λ<sub>max.</sub> 238, 298, and

471 nm (ε 5 880, 31 800, and 3 620); ν<sub>max.</sub> 1 500 and 2 200 cm<sup>-1</sup>; τ 1.7—2.4 (m, ArH).

**2,3-Diphenyl-1,2,3,4-tetrazolium-5-olates (8).**—Pentyl nitrite (7.5 g) was added to a solution of 3-nitro-1,5-diphenylformazan (14) (2.0 g)<sup>6</sup> and glacial acetic acid (7.5 g) in acetone (75 ml) and the mixture was heated under reflux (40 min). After cooling to 0°, ether was added and a pale yellow solid separated. This product was washed with ether, recrystallised from ethanol-ether, and identified as 2,3-diphenyl-1,2,3,4-tetrazolium-5-olate (8) (1.4 g, 79%), needles, m.p. 175° (lit.,<sup>6</sup> 176°) (Found: C, 65.2; H, 4.3; N, 23.6%; M<sup>+</sup>, 238. Calc. for C<sub>13</sub>H<sub>10</sub>N<sub>4</sub>O: C, 65.5; H, 4.2; N, 23.5%; M, 238); λ<sub>max.</sub> 233 and 331 nm (ε 11 100 and 5 058); ν<sub>max.</sub> 1 655 cm<sup>-1</sup>; τ 2.3—2.9 (m, ArH).

**2,3-Diphenyl-1,2,3,4-tetrazolium-5-thiolate (9).**—Dithizone (15)<sup>6</sup> (2.0 g) in acetone (150 ml) was gently heated on a steam-bath (5 min) with manganese dioxide (6.0 g). The hot solution was filtered and concentrated giving red needles. After washing with acetone and recrystallisation from acetone-ether, the product was identified as 2,3-diphenyl-1,2,3,4-tetrazolium-5-thiolate (9) (1.5 g, 75%), red needles, m.p. 180° (lit.,<sup>6</sup> 180.5°) (Found: C, 61.4; H, 4.1; N, 22.1; S, 12.6%; M<sup>+</sup>, 284. Calc. for C<sub>13</sub>H<sub>10</sub>N<sub>4</sub>S: C, 61.4; H, 3.9; N, 22.0; S, 12.6%; M, 284); λ<sub>max.</sub> 414 and 255 nm (ε 11 320 and 23 900); ν<sub>max.</sub> (KBr) 977, 1 110, 1 310, 1 455, and 1 480 cm<sup>-1</sup>; τ(CDCl<sub>3</sub> + CF<sub>3</sub>-CO<sub>2</sub>H) 2.4 (s, ArH).

**5-Ethoxy-2,3-diphenyl-1,2,3,4-tetrazolium Tetrafluoroborate (10).**—2,3-Diphenyl-1,2,3,4-tetrazolium-5-olate (8) (1.2 g) was added to a solution of triethyloxonium tetrafluoroborate (1.0 g)<sup>11</sup> in dichloromethane (10 ml) and the mixture set aside at room temperature (12 h). Addition of ether, with ice cooling, gave a crystalline precipitate which was recrystallised from acetone-ether giving 5-ethoxy-2,3-diphenyl-1,2,3,4-tetrazolium tetrafluoroborate (10) (1.6 g, 89%) as prisms, m.p. 213° (Found: C, 50.8; H, 4.5; N, 16.05. C<sub>15</sub>H<sub>15</sub>BF<sub>4</sub>N<sub>4</sub>O requires C, 50.9; H, 4.2; N, 15.8%); λ<sub>max.</sub> 265 and 292 nm (ε 5 996 and 6 439); ν<sub>max.</sub> (Nujol) 1 000—1 130br and 1 575 cm<sup>-1</sup>; τ(CDCl<sub>3</sub> + CF<sub>3</sub>-CO<sub>2</sub>H), 2.39 (s, 10 ArH), 5.22 (q, J 6 Hz, OCH<sub>2</sub>Me), and 8.42 (t, J 6 Hz, OCH<sub>2</sub>Me); m/e, 267 (M<sup>+</sup> - BF<sub>4</sub>).

**2,3-Diphenyl-5-ethylthio-1,2,3,4-tetrazolium tetrafluoroborate (12; R = Et, X = BF<sub>4</sub>)** was prepared similarly (0.6 g, 82%), prisms, m.p. 213° (Found: C, 48.8; H, 4.1; N, 15.2; S, 8.7. C<sub>15</sub>H<sub>15</sub>BF<sub>4</sub>N<sub>4</sub>S requires C, 48.6; H, 4.1; N, 15.15; S, 8.7%); λ<sub>max.</sub> 343, 257, and 231 nm (ε 5 471, 6 753, and 24 240); ν<sub>max.</sub> (KBr) 1 000—1 200br, 1 450, and 1 480 cm<sup>-1</sup>; τ(CDCl<sub>3</sub> + CF<sub>3</sub>-CO<sub>2</sub>H) 2.38 (s, 10 ArH), 6.59 (q, J 6 Hz, SCH<sub>2</sub>Me), and 8.49 (t, J 6 Hz, SCH<sub>2</sub>Me); m/e, 283 (M<sup>+</sup> - BF<sub>4</sub>).

**3-Ethoxy-1,5-diphenylformazan (11; R = Et).**—Sodium sulphide (0.66 g) in water (3 ml) was added to a solution of compound (10) (1.0 g) in warm ethanol (50 ml). The resulting dark mixture was warmed on a steam-bath (5 min) and then poured into water (150 ml). The solid product which separated on standing (12 h) was washed with water, recrystallised from acetone-water, and identified as 3-ethoxy-1,5-diphenylformazan (11; R = Et) (0.7 g, 92%), golden-brown needles, m.p. 86° (Found: C, 67.3; H, 6.2; N, 21.1%; M<sup>+</sup>, 268. C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O requires C, 67.2; H, 6.0; N, 20.9%; M, 268); λ<sub>max.</sub> 258, 295, and 433 nm (ε 15 540, 8 308, and 26 800); ν<sub>max.</sub> 1 140—1 180br, 1 496, 1 555, 1 595, 2 950, and 3 310 cm<sup>-1</sup>; τ 1.45 (s, NH, exchanged by D<sub>2</sub>O), 1.95—3.2 (m, 10 ArH), 5.42—5.90 (q, J 6 Hz, OCHMe), and 8.3—8.75 (t, J 6 Hz, OCH<sub>2</sub>Me).

In a similar manner, 3-ethylthio-1,5-diphenylformazan (13; R = Et) (0.2 g, 87%), dark brown, lustrous needles, m.p. 84° (decomp.) (lit.,<sup>13</sup> 70°), was prepared (Found: C, 63.1; H, 5.6; N, 19.9; S, 11.35%;  $M^+$ , 284. Calc. for  $C_{15}H_{16}N_4S$ : C, 63.4; H, 5.6; N, 19.7; S, 11.3%;  $M$ , 284;  $\lambda_{\max}$ , 270, 413, and 535 nm (13 380, 22 250, and 4 319);  $\nu_{\max}$ , 1 130—1 150, 1 395, 1 520, 1 600, 2 950, and 3 200  $cm^{-1}$ ;  $\tau$  2.0—2.7 [m, 10 ArH + 1 NH (exchanged by  $D_2O$ )], 6.75—7.25 (q,  $J$  6 Hz,  $SCH_2Me$ ), and 8.4—8.9 (t,  $J$  6 Hz,  $SCH_2Me$ ).

3-Methylthio-1,5-diphenylformazan (13; R = Me).—5-Methylthio-2,3-diphenyl-1,2,3,4-tetrazolium iodide (12; R = Me, X = I)<sup>8</sup> was treated with sodium sulphide under the conditions just described. The product was identified as 3-methylthio-1,5-diphenylformazan (13; R = Me) (0.2 g, 59%), dark brown needles, m.p. 134° (lit.,<sup>13</sup> 127—129°) (Found: C, 62.1; H, 5.4; N, 21.0; S, 12.0%;  $M^+$ , 270. Calc. for  $C_{14}H_{14}N_4S$ : C, 62.2; H, 5.2; N, 20.7; S, 11.7%;  $M$ , 270);  $\nu_{\max}$ , 1 495—1 520br, and 1 600  $cm^{-1}$ ;  $\tau$  2.2—2.8 [m, 10 ArH + 1 NH (exchanged by  $D_2O$ )] and 7.5 (s, Me).

[6/1146 Received, 15th June, 1976]

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