Oxidation of methyl groups in the reaction of sulfur homopolyatomic cations with acetonitrile: formation and crystal structure of the novel trithietanylium ring

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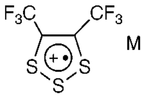
RCN (R = C_6F_5, Me) reacts with $S_n(AsF_6)_2$ (n = 4, 8) in liquid SO_2 to give the corresponding 3,5-disubstituted-1,2,4 thiadiazoles, and also, in the MeCN case, the tricyclic trication 4 containing the trithietanylium $\text{-}\overline{CSSS}^+$ and 1,2,3-dithiazolium $\text{-}\overline{CSSNC}H^+$ rings formed by the oxidation of methyl groups by sulfur homopolyatomic cations.

The isolation of stable soluble salts of the homopolyatomic cations of groups16 and 17[1] has allowed the exploration of their chemistry, leading to new classes of compounds.[2] Reactions of sulfur cations with F_3CCCCF_3 and CF_3CN gave the new radical cations $F_3C\overline{CSSSC}CF_3^{+\cdot}$ **1** and $F_3C\overline{CNSSS}^{+\cdot}$ quantitatively,[3] and with dicyanogen the diradical $^{+\cdot}\overline{SSSNC}\,\overline{CNSSS}^{+\cdot}$.[4] In an attempt to probe the generality of such reactions, we found that with C_6F_5CN, **2a** and **2b** were obtained, and with MeCN, derivatives of **3a** were formed. This furnishes a new, simple, high yield synthetic route to 3,5-disubstituted 1,2,4-thiadiazoles from nitriles with relatively low ionisation energies.[5]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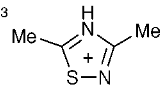
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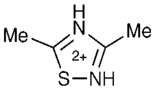
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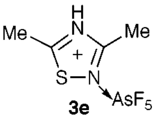
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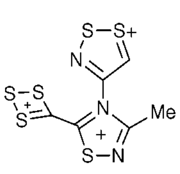
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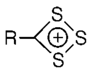
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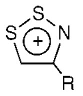
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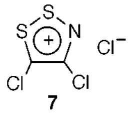
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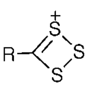
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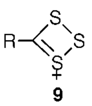
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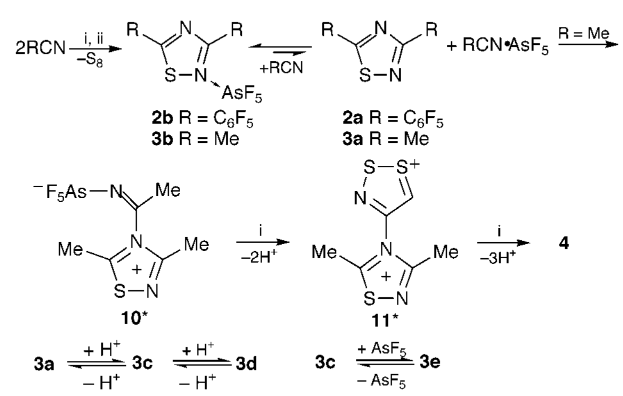
The reaction of an equal molar mixture of $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$ with MeCN gives the AsF_6^- salt of **4**, as well as AsF_6^- salts of **3c**, **3d** and **3e**. Species **4** contains the trithietanylium ring **5**, the first example of the $\text{-}\overline{CXXX}^+$ (X = O, S, Se, and Te) heterocyclic ring system, and a 1,2,3-dithiazolium ring **6**, formed by the oxidation of the methyl groups by sulfur cations and transfer of the protons to **3a** (Scheme 1). This reaction is reminiscent of the oxidation of $ArCH_3$ to $ArCO_2H$ by strong oxidising reagents.[6] The synthesis of the chloride of **5** (R = Ph) has been claimed,[7] but no structural evidence has been reported. Fused derivatives of **6**, Herz salts, are well known,[8] and recently, the X-ray structure of **7** (Appel's salt) was determined.[9]

The structures of **2b**† and the AsF_6^- salts of **3c**,‡ **3e**§ and **4**¶ were determined by X-ray crystallography. Species **4** dimerises by weak electrostatic interactions [S(5)–N(4a) 2.946(6) Å]. The centrosymmetric dimer is shown in Fig. 1. All rings are planar, and calculated (at MPW1PW91/6-31G* level)‖ distances and



Scheme 1 *Reagent and condition*: i, $S_n(AsF_6)_2$ (n = 4 or 8); ii, liquid SO_2. * = Proposed intermediates.

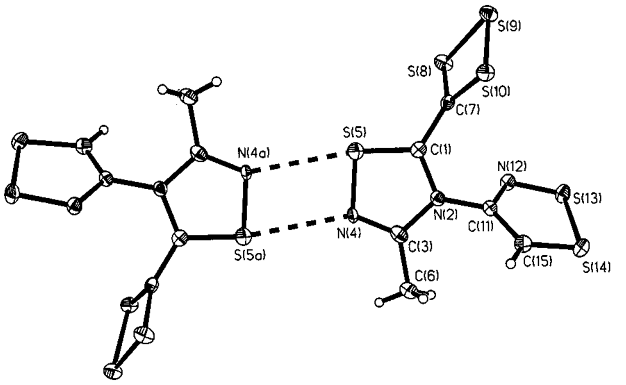
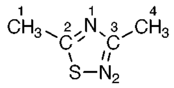


Fig. 1. ORTEP of **4** drawn at the 50% probability level. Selected bond lengths (Å), and angles (°); calculated results (MPW1PW91/6–31G*) are given in parentheses and in bold. C(1)–N(2) 1.377(7) (**1.367**), N(2)–C(3) 1.384(8) (**1.417**), C(3)–N(4) 1.332(8) (**1.300**), N(4)–S(5) 1.676(5) (**1.630**), S(5)–C(1) 1.663(6) (**1.697**), C(3)–C(6) 1.500(9) (**1.484**), C(1)–C(7) 1.450(8) (**1.451**), C(7)–S(8) 1.686(6) (**1.703**), S(8)–S(9) 2.046(2) (**2.064**), S(9)–S(10) 2.057(2) (**2.067**), S(10)–C(7) 1.692(6) (**1.705**), N(2)–C(11) 1.443(7) (**1.430**), C(11)–N(12) 1.335(7) (**1.319**), N(12)–S(13) 1.579(5) (**1.600**), S(13)–S(14) 2.041(2) (**2.063**), S(14)–C(15) 1.664(6) (**1.669**), C(15)–C(11) 1.398(8) (**1.409**); C(1)–N(2)–C(3) 111.1(5) (**111.8**), N(2)–C(3)–N(4) 115.2(5) (**113.4**), C(3)–N(4)–S(5) 109.2(4) (**112.3**), N(4)–S(5)–C(1) 94.3(3) (**94.4**), S(5)–C(1)–N(2) 110.0(4) (**108.2**), C(1)–N(2)–C(11) 122.0(5) (**126.1**), C(11)–N(2)–C(3) 126.6(5) (**122.1**), N(2)–C(3)–C(6) 122.6(6) (**124.3**), C(6)–C(3)–N(4) 122.2(6) (**122.4**), S(5)–C(1)–C(7) 123.3(4) (**122.0**), N(2)–C(1)–C(7) 126.7(5) (**129.8**), C(1)–C(7)–S(8) 124.9(4) (**123.2**), S(8)–(C7)–S(10) 107.0(3) (**106.6**), C(7)–S(8)–S(9) 85.3(2) (**85.4**), S(8)–S(9)–S(10) 82.86(8) (**82.8**), S(9)–S(10)–C(7) 84.8(2) (**85.2**), S(10)–C(7)–C(1) 127.4(4) (**129.5**), C(11)–N(12)–S(13) 115.5(4) (**116.5**), N(12)–S(13)–S(14) 98.2(2) (**97.5**), S(13)–S(14)–C(15) 93.0(2) (**92.4**), S(14)–C(15)–C(11) 114.4(4) (**115.4**), C(15)–C(11)–N(12) 118.9(5) (**118.2**), N(2)–C(11)–N(12) 116.9(5) (**118.6**), C(15)–C(11)–N(2) 124.2(5) (**123.2**).

Table 1 Observed[a] and calculated[b] (in parentheses) ^1H and ^{13}C NMR chemical shifts of **3a** derivatives



Deriv-ative	δ_H C1-H	C4-H	N1-H	N2-H	δ_C C1	C2	C3	C4
3a	2.73 (2.69)	2.53 (2.47)	—	—	15.4 (18.6)	187.9 (196.6)	173.3 (182.0)	17.4 (19.7)
3c	3.07 (3.05)	2.75 (2.89)	12.33 (9.69)	—	14.3 (16.0)	192.9 (205.0)	164.3 (173.5)	15.5 (16.9)
3d[c]	3.50 (3.85)	3.35 (3.66)	13.21 (10.50)	12.93 (10.10)	17.0 (21.1)	196.1 (214.4)	170.9 (185.3)	15.6 (19.5)
3e[c]	3.39 (3.09)	3.24 (3.47)	12.74 (9.47)	—	15.8 (16.6)	193.7 (202.7)	169.0 (175.6)	16.3 (18.3)

[a] Chemical shifts were obtained at −70 °C in liquid SO_2, using $NH_4(AsF_6)$ (δ_H 5.80) or $MeCN{\cdot}AsF_5$ (δ_H 2.67, δ_C 110.7) as internal standards. [b] Isotropic NMR shielding tensors were calculated at the MPW1PW91/6-311G(2DF)//MPW1PW91/3-21G* level and referenced against calculated TMS values. [c] ^1H and ^{13}C chemical shifts were assigned based on HMQC and HMBC experiments at −70 °C.

bond angles are in good agreement with the values derived from the X-ray structure. The structure of the observed 1,2,4-thiadiazolium ring fragment in **4** does not differ significantly from that in **3c** and **3e**. Although the $-\overline{CSSS}^+$ ring is formally related to the 6π square planar S_4^{2+} ring,[1] the cyclobutadiene dianion,[10] and 1,2-dithietes,[11] it can be represented by the valence bond structures **8** and **9**, consistent with the average Pauling bond orders of 1.35 (C–S) and 1.06 (S–S).

C_6F_5CN (3.283 g; 17.00 mmol) reacted with $S_4(AsF_6)_2$[12] (2.198 g; 4.344 mmol) in SO_2 (11.917 g) in a two-bulb Pyrex glass vessel incorporating a medium sintered-glass frit (apparatus and techniques given in ref. 12). After 3 days, insoluble S_8 (FT-Raman), OSF_2, AsF_3 (gas phase IR and ^{19}F NMR), 5.136 g of a mixture of **2a** (elemental analysis, ^{19}F NMR) and **2b** (elemental analysis, ^{19}F NMR, X-ray crystal structure, MS, IR and FT-Raman), and $S_n(AsF_6)_2$ ($n \approx 19$) (colour, EPR) were identified.**

The AsF_6^- salts of **3c**, **3e** and **4** were prepared by the reaction of MeCN (0.5108 g; 12.443 mmol) and an equal molar mixture of $S_n(AsF_6)_2$ ($n = 4, 8$) [prepared by the reaction of S_8 (1.0222 g; 31.878 mmol) and AsF_5 (2.6668 g; 15.694 mmol) in SO_2 (12.991 g)][3] for about 15 days under strictly anhydrous conditions.[12] The overall molar ratio of MeCN, $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$ was 4:1:1. After slowly removing the solvent and washing out the most soluble products (minor), the obtained mixture contained significant amounts of white needle-like crystals of the AsF_6^- salt of **3e** and dark red brick-like crystals of the AsF_6^- salt of **4**. The mixture was dissolved in SO_2, leaving insolubles (including the AsF_6^- salt of **4** and S_8), and the obtained solubles were identified as a mixture of the AsF_6^- salts of **3c**, **3d** and **3e** by multinuclear NMR studies, here and in related studies. Observed and calculated NMR results are in reasonable agreement (Table 1). OSF_2 and AsF_3 (^{19}F NMR) and minor amounts of deprotonated species (*in situ* ^{13}C studies) were also identified. The formation of S_8 indicates that sulfur cations were reduced during the deprotonation process of the methyl groups. In a related reaction of $S_4(AsF_6)_2$ and **3a**,†† crystals of the AsF_6^- salt of **3c** were obtained and the X-ray crystal structure determined.

Hitherto the chemistry of homopolyatomic sulfur and selenium cations has been restricted to hydrogen-free compounds with the exception of a preliminary report of the reaction of E_n^{2+} (E = S, Se, $n = 4, 8$) with alkanes and toluene giving products that included sulfides and selenides.[13] This work suggests an extensive novel organic chemistry of homopolyatomic cations of group 16, presently under investigation.

We thank Dr Ingo Krossing for valuable advice on the theoretical calculations, Dr Larry Calhoun (UNB) for his assistance with numerous NMR experiments, Dr J. Britten (McMaster University) for X-ray data collection on species **3e** AsF_6 and **4** $(AsF_6)_3$, and NSERC for an operating grant (J. P.).

Notes and references

† *Crystal data* for **2b**: $C_{14}AsF_{15}N_2S$, $M = 588.14$, monoclinic ($C2/c$), $a = 11.967(4)$, $b = 12.268(4)$, $c = 24.076(5)$ Å, $\beta = 96.66(3)°$, $U = 3511(2)$ Å^3, $D = 2.225$ g cm^{-3}, $T = 293(2)$ K, $F(000) = 2256$, $Z = 8$, $\mu = 2.216$ mm^{-1}, 6593 reflections measured, 3093 independent reflections, $R1$ ($wR2$) = 0.0538 (0.1347).

‡ *Crystal data* for **3c** AsF_6: $C_4H_7AsF_6N_2S$, $M = 304.10$, orthorhombic, space group $Pbca$, $a = 11.874(3)$, $b = 12.617(3)$, $c = 13.005(3)$ Å, $U = 1948.3(9)$ Å^3, $Z = 8$, $D = 2.073$ g cm^{-3}, $T = 150(2)$ K, $F(000) = 1184$, $\mu = 3.757$ mm^{-1}. 3649 reflections measured, 1725 independent reflections, $R1$ ($wR2$) = 0.0433 (0.0737).

§ *Crystal data* for **3e** AsF_6: $C_4H_7As_2F_{11}N_2S$, $M = 474.04$, orthorhombic, space group $Pnma$, $a = 14.746(3)$, $b = 8.023(2)$, $c = 11.034(2)$ Å, $U = 1305.4(5)$ Å^3, $Z = 4$, $D = 2.412$ g cm^{-3}, $T = 210(2)$ K, $F(000) = 904$, $\mu = 5.402$ mm^{-1}. 13468 reflections measured, 1502 independent reflections, $R1$ ($wR2$) = 0.0262 (0.0615).

¶ *Crystal data* **4** $(AsF_6)_3$: $C_6H_4As_3F_{18}N_3S_6$, $M = 877.24$, monoclinic, space group $P2_1/n$, $a = 13.9666(1)$, $b = 10.6426(1)$, $c = 16.5839(1)$ Å, $\beta = 111.285(1)°$, $U = 2296.90(3)$ Å^3, $Z = 4$, $D = 2.537$ g cm^{-3}, $T = 153$ K, $F(000) = 1672$, $\mu = 5.034$ mm^{-1}. 24701 reflections measured, 5200 independent reflections, $R1$ ($wR2$) = 0.0593 (0.1499). The hydrogen atoms were found in difference Fourier maps and included into the refinement by a riding model. CCDC 182/1336. See http://www.rsc.org/suppdata/cc/1999/1801/ for crystallographic data in .cif format.

‖ All calculations were performed with GAUSSIAN 98W. (ref. 14). MPW1PW91 is a hybrid HF-DFT method. (ref. 15). Calculated distances and angles and observed values are in good agreement for **3c** and **3e**.

** Similar results were obtained from reaction of C_6F_5CN with an equal molar mixture of $S_n(AsF_6)_2$ ($n = 4, 8$).

†† Species **3a** was synthesised according to ref. 16.

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