The Preparation and *X*-Ray Crystal Structures of 4-Methyl-1,3,2-dithiazolium Hexafluoroarsenate(V) and 5-Methyl-1,3,2,4-dithiadiazolium Hexafluoroarsenate(V) and their Reduction to Stable Free Radicals

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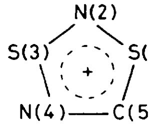
Acetonitrile, propyne, and acetylene react essentially quantitatively with S_2NAsF_6 to give the hexafluoroarsenate salts of 5-methyl-1,3,2,4-dithiadiazolium, 4-methyl-1,3,2-dithiazolium, and 1,3,2-dithiazolium respectively, the structures of the former two salts being determined by *X*-ray crystallography; the cations have been reduced chemically and electrolytically to form long-lived free radicals identified by their e.s.r. spectra.

The dithionitronium hexafluoroarsenate(V) S_2NAsF_6[1] is a useful building block in sulphur–nitrogen chemistry. This is illustrated by its essentially quantitative reaction with neat acetonitrile to give the hexafluoroarsenate salt of the 5-methyl-1,3,2,4-dithiadiazolium (**1**) cation, and with a slight excess of acetylene or propyne in liquid sulphur dioxide to form the hexafluoroarsenate salts of the 1,3,2-dithiazolium (**2**) and 4-methyl-1,3,2-dithiazolium (**3**) cations respectively.

The 1,2,3,5-dithiadiazolium cations,[2] isomeric with (**1**), containing a disulphide group are well known, and fluorosulphate salts of 5-acylimino-1,3,2,4-dithiadiazolium[3] cations, related to (**1**), have been prepared. Cations like (**2**) and (**3**) containing the 1,3,2-dithiazolium ring appear not to have been previously reported, although the related neutral species, 2-phenyl-5-methyl-1,3,2-benzodithiazole,[4] and the cations 6-chloro-1,2,3-benzodithiazolium[5] and 3,5-diphenyl-1,2,4-dithiazolium,[6] with the heterocyclic ring isomeric with (**2**) and (**3**), containing a disulphide group are known. The reaction of S_2N^+ with MeCN and RC≡CH (R = Me or H) are examples of general routes to cations containing the 1,3,2,4-dithiadiazolium and 1,3,2-dithiazolium rings, and they themselves are potentially useful intermediates. This is illustrated by the reduction of (**1**) to give the stable free radical 5-methyl-1,3,2,4-dithiadiazol-2-yl (**4**) reported below.

The hexafluoroarsenate salts of (**1**), (**2**), and (**3**) were characterised by elemental analysis, and i.r. and Raman spectroscopy. Colourless crystals suitable for *X*-ray analysis of (**1**) and (**3**) were grown from SO_2–SO_2ClF solutions.

Crystal data: (**1**), $C_2H_3S_2N_2AsF_6$, $M = 308.09$, monoclinic, space group $P2_1/c$, $a = 8.182(7)$, $b = 9.822(3)$, $c = 11.515(7)$ Å, $\beta = 110.91(6)°$, $U = 864$ Å^3, $Z = 4$, $D_c = 2.37$ Mg m^{-3}, μ(Mo-K_α) = 4.44 mm^{-1}, λ(Mo-K_α) = 0.71069 Å, $T = 100$ K. Data were collected for $5° \leqslant 2\theta \leqslant 45°$, 1391 unique reflections, 893 observed [$I \geqslant 2\sigma(I)$]. Data were initially collected at room temperature and the structure was solved by direct methods; the resulting structure did not refine well, the light atoms exhibiting very large anisotropic thermal motions. Recollection of the data at 100 K partially reduced this effect and resulted in final residuals of $R = 0.12$, $R_w = 0.13$. *Crystal data:* (**3**), $C_3H_4S_2NAsF_6$, $M = 307.10$, monoclinic, space group $P2_1/c$, $a = 8.539(5)$, $b = 9.941(2)$, $c = 12.053(5)$ Å, $\beta = 116.69(4)°$, $U = 914$ Å^3, $Z = 4$, $D_c = 2.23$ Mg m^{-3}, μ(Mo-K_α) = 4.19 mm^{-1}, λ(Mo-K_α) = 0.71069 Å, $T = 293$ K. Data were collected for $5° \leqslant 2\theta \leqslant 45°$, 1612 unique reflections, 1077 observed [$I \geqslant 2\sigma(I)$]. The structure was solved by direct methods and refined by least squares to final residuals of $R = 0.062$, $R_w = 0.096$.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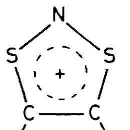
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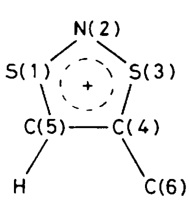
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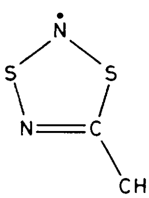
(4)

Both salts are essentially ionic with some anion–cation interaction. Both cations are planar, including the carbons of the methyl substituents. The cation bond lengths and angles are given in Table (1).†

Our MO calculations indicate that the heterocyclic cations have some aromatic character but not sufficient to prevent easy reduction. Consequently, silver powder was added to a solution of (**1**) in acetonitrile and the resulting solution gave the e.s.r.

Table 1. Bond distances (Å) and angles (°) for the cations of (**1**) and (**3**).[a]

$C_2H_3S_2N_2AsF_6$ (**1**)		$C_3H_4S_2NAsF_6$ (**3**)	
S(1)–N(2)	1.61(2)	S(3)–N(2)	1.620(10)
N(2)–S(3)	1.60(2)	N(2)–S(1)	1.580(10)
S(3)–N(4)	1.58(2)	S(1)–C(5)	1.673(11)
N(4)–C(5)	1.33(3)	C(5)–C(4)	1.365(14)
C(5)–S(1)	1.75(2)	C(4)–S(3)	1.696(11)
C(5)–C(6)	1.44(3)	C(4)–C(6)	1.460(14)
C(5)–S(1)–N(2)	99(1)	C(4)–S(3)–N(2)	100.9(5)
S(1)–N(2)–S(3)	111(1)	S(3)–N(2)–S(1)	112.4(6)
N(2)–S(3)–N(4)	104(1)	N(2)–S(1)–C(5)	101.4(5)
S(3)–N(4)–C(5)	115(2)	S(1)–C(5)–C(4)	114.0(8)
N(4)–C(5)–S(1)	112(2)	C(5)–C(4)–S(3)	111.2(8)
N(4)–C(5)–C(6)	127(2)	C(5)–C(4)–C(6)	128.5(1.0)
S(1)–C(5)–C(6)	122(2)	S(3)–C(4)–C(6)	120.2(8)

[a] Estimated standard deviations in parentheses.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

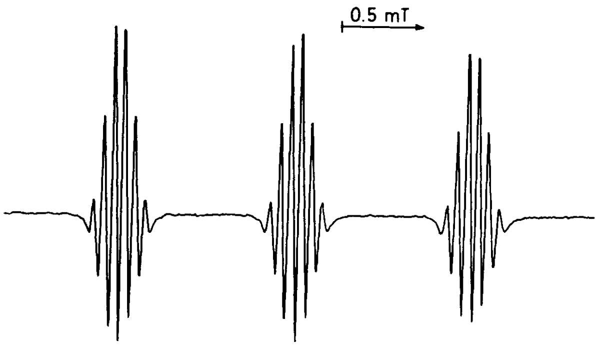

Figure 1. The second-derivative X-band e.s.r. spectrum of the radical (**4**) in acetonitrile at −51.9 °C (a^{N2} = 1.095 mT, a^{N4} = 0.0644 mT, $a^{H}_{CH_3}$ = 0.0644 mT).

spectrum shown in Figure 1. The spectrum (recorded at low temperature for optimum resolution) can be attributed to the long-lived 5-methyl-1,3,2,4-dithiadiazol-2-yl free radical (**4**).

Radical (**4**) is a close analogue of a new class of free radicals we have prepared[7] by the cycloaddition of tetrasulphur dinitride to acetylenes; for example, it does not dimerise even at −100 °C. The intriguing difference between the two approaches is that radicals cannot be prepared by the cycloaddition of S_4N_2 to MeCN, HC≡CH and MeC≡CH, although some other acetylenes RC≡CR (R = Ph, CO_2Me, or CF_3) did give analogous radicals. Another useful way to reduce the salts to radicals is to add sodium dithionite to solutions of them in tetrahyrofuran. Excess of salt has to be avoided if excessive line broadening is not to occur in the e.s.r. spectra. We have confirmed by cyclic voltammetry that rapid electron exchange occurs. Solutions of the heterocyclic cations in acetonitrile give clearly reversible cyclic voltammograms: the redox potentials are −0.26, +0.02, and −0.63 V respectively for compounds (**1**), (**2**) and (**3**) when measured against an Ag/Ag$^+$ (0.01 M in acetonitrile) reference electrode.

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