

Preparation of 1,3,2-Dithiazolium Hexafluoroarsenate(v), Preparation and Crystal Structures of 5-Methyl-1,3,2,4-dithiadiazolium and 4-Methyl-1,3,2-dithiazolium Hexafluoroarsenate(v) and the Reduction of These Salts to Stable Free Radicals†

Gregory K. MacLean, Jack Passmore,* M. N. Sudheendra Rao, Melbourne J. Schriver, and Peter S. White*

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

Donald Bethell, Roger S. Pilkington, and Leslie H. Sutcliffe*

Department of Chemistry, University of Liverpool, Donnan Laboratories, Liverpool L69 3BX

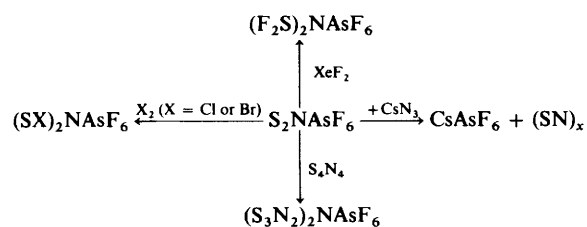
Crystalline $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$, $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$, and $\text{H}\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ were prepared in essentially quantitative yield by the reaction of S_2NAsF_6 with CH_3CN , CH_3CCH , and HCCH respectively, in sulphur dioxide solution. The compounds have been characterised by elemental analysis, i.r. and mass spectrometry. The compound $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ crystallizes in the monoclinic space group $P2_1/c$, with unit-cell dimensions $a = 8.182(7)$, $b = 9.822(3)$, $c = 11.515(7)$ Å, $\beta = 110.91(6)^\circ$, and $Z = 4$. The structure was solved from low-temperature diffractometer data by direct methods and refined by least-squares techniques to a final R of 0.12 for 893 observed reflections. The structure consists of discrete, planar $\text{CH}_3\overline{\text{CSNSN}}^+$ cations and AsF_6^- anions with some cation-anion interactions. The compound $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ crystallizes in the monoclinic space group $P2_1/c$, with unit-cell dimensions $a = 8.539(5)$, $b = 9.941(2)$, $c = 12.053(5)$ Å, $\beta = 116.69(4)^\circ$, and $Z = 4$. The structure was solved by direct methods and refined by least-squares techniques to a final R of 0.049 for 1 077 observed reflections. The structure contains the hitherto unknown $\text{CH}_3\overline{\text{CSNSCH}}^+$ cation and the AsF_6^- anion with some cation-anion interaction. Both $\text{CH}_3\overline{\text{CSNSN}}^+$ and $\text{H}\overline{\text{CSNSCR}}^+$ ($R = \text{H}$ or CH_3) can be regarded as 6π cyclic systems. The cations have been reduced chemically and electrolytically to form long-lived free radicals identified by their e.s.r. spectra; INDO calculations have yielded values of hyperfine coupling constants in good agreement with those obtained experimentally.

We have developed a simple convenient synthesis of S_2NAsF_6 containing the S_2N^+ cation (*cf.* NO_2^+) that is proving to be a useful building block to other sulphur-nitrogen species (see Scheme).¹ We report herein the reaction of S_2NAsF_6 with the unsaturated species CH_3CN , CH_3CCH , and HCCH leading to the hexafluoroarsenate(v) salts of (1), (2), and (3) respectively.

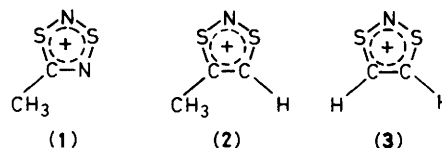
Cations like (2) and (3) containing the 1,3,2-dithiazolium ring have not been reported, although the related neutral molecules 5-methyl-2-phenylbenzo-1,3,2-dithiazole (4),² compound (5), containing the $\overline{\text{CSNSC}}$ ring,³ and the disulphide isomers (6) and (7) are also known.^{4,5} A cation containing the 1,3,2,4-dithiadiazolium ring [as in (1)] has recently been reported as 5-bromothio-1,3,2,4-dithiadiazolium, (8).⁶

We previously gave a brief account of the synthesis of the 4-methyl-1,2,3,5-dithiadiazolium cation, (9), an isomer of (1).⁷ We include below an improved, but low yield, route to (9) as the chloride salt. It has recently been prepared independently by a different route.⁸ Various other derivatives of (9) are well characterised.⁹⁻¹²

We have also previously reported^{13,14} that some alkynes react thermally with tetrasulphur dinitride to give long-lived free radicals believed to have the structure (10), where $R^1, R^2 = \text{C}_6\text{H}_5, \text{C}_6\text{H}_5, \text{CO}(\text{O})\text{CH}_3, \text{CO}(\text{O})\text{CH}_3, \text{CF}_3, \text{CF}_3, \text{CF}_3, \text{H}; \text{CH}_3, \text{CH}_3; (\text{CH}_3)_3\text{C}, (\text{CH}_3)_3\text{C}; \text{C}_6\text{H}_5, \text{CH}_3; \text{CH}_3, \text{CO}(\text{O})\text{CH}_3$; or $\text{C}_6\text{H}_5\text{C}\equiv\text{C}, \text{C}_6\text{H}_5$. It was not possible to obtain radicals with hydrogen as a substituent, apart from the single example where $R^1, R^2 = \text{CF}_3, \text{H}$. However, we have discovered¹⁵ that the hexafluoroarsenate salts of (2) and (3) can be reduced to give



Scheme. Some reactions of $\text{S}_2\text{N}^+\text{AsF}_6^-$



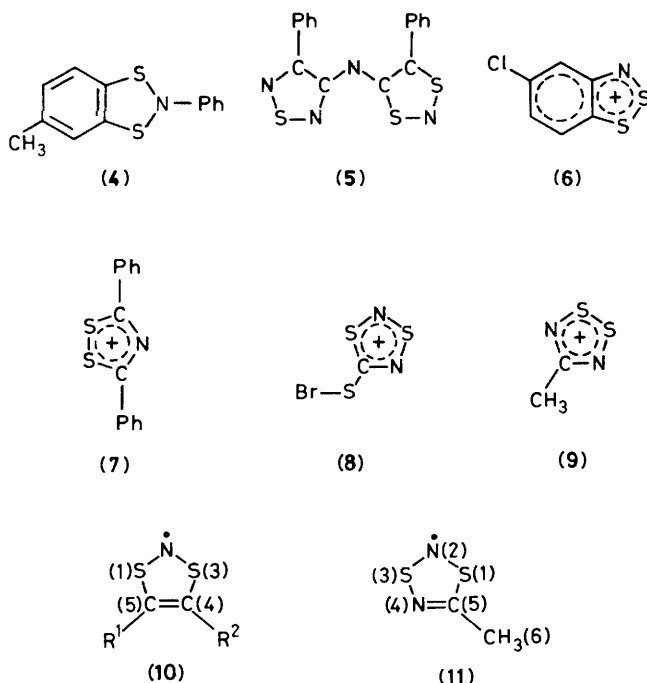
radicals of type (10), thus confirming our belief that the structural parameters of the dithiazolium rings are closely related to those of the dithiazolium ring.¹⁴ Furthermore, another new type of free radical can be prepared from the hexafluoroarsenate salt of (1), namely (11). We have been unable to prepare this radical by the thermal reaction of tetrasulphur dinitride with acetonitrile.

It is possible that these reactions are general and therefore a variety of other derivatives of (10) and (11) may be prepared from S_2N^+ , *via* cations analogous to (1), (2), and (3), followed by suitable reduction to the corresponding neutral radicals.

INDO and Gaussian 76 molecular-orbital calculations have been used to find the optimised geometry of the 1,3,2-dithiazolium and 1,3,2,4-dithiadiazolium cations and the data

† Supplementary data available (No. SUP 56196, 4 pp); thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii-xix. Structure factors are available from the editorial office.

Non-S.I. units employed: eV $\approx 1.60 \times 10^{-19}$ J, Torr ≈ 133 Pa.



obtained have been compared with the experimental values obtained by *X*-ray crystallography. INDO calculations on these structures were then used to calculate the e.s.r. coupling constants of the corresponding radicals. The good agreement of the coupling constants with the experimental results suggests that the structure of a cation and its cognate free radicals are very similar. This conclusion led us to carry out cyclic voltammetry measurements on the salts. A preliminary account of this work has been reported.¹⁵

Experimental

Preparation of Hexafluoroarsenate Salts of (1), (2), and (3).—Apparatus, techniques, and chemicals, unless specified, have been described in refs. 1 and 7. S_2NaAsF_6 was prepared as in ref. 1. $HCCl_3$ (Canadian Liquid Air) was stored over freshly regenerated 3A molecular sieves (J. T. Baker Chemical Co.) in a Monel container, CH_3CCH_3 (Albany International) was used without purification, and SO_2Cl_2 (Aldrich) was stored over solid NaF. Fisher high-performance liquid chromatography grade acetonitrile was dried over 3A molecular sieves, distilled and then stored over freshly-dried 3A molecular sieves. Reactions were carried out in Pyrex, two-bulbed (*ca.* 15 cm³) vessels incorporating a coarse glass frit and a J. Young, Teflon in glass, valve. All reported melting and decomposition points are uncorrected.

Preparation of $CH_3CSNSN^+AsF_6^-$ (1). In a typical reaction CH_3CN (1.72 g, 41.9 mmol) was condensed onto S_2NaAsF_6 (1.16 g, 9.33 mmol). A deep orange-red solution was formed initially, which turned orange-yellow on reaching room temperature. Excess CH_3CN was removed under dynamic vacuum after 1 h, and an $SO_2-SO_2Cl_2$ mixture (11.29 g, 2:1 mol ratio) was added to the pale yellow solid (1.34 g). The solution was filtered through the frit and the solvent condensed back onto the previously undissolved solid. The process was repeated three times effecting quantitative transfer. The solvent was slowly condensed into the other bulb by cooling in a cold water-bath ($T \approx 0^\circ C$). The resulting needle-shaped crystals were quickly washed with 2–3 cm³ of solvent giving colourless crystals (1.25 g, 4.07 mmol; 94% yield based on $CH_3CSNSN^+AsF_6^-$),

and a more soluble yellow-brown solid (0.09 g). Single crystals suitable for *X*-ray analysis were glued [Loctite Superbond (5–15 sec)] on a glass fibre in a dry-nitrogen filled glove bag before being flame sealed inside a glass capillary. The yellow-brown solid contained a mixture of $CH_3CSNSN^+AsF_6^-$ and traces of hydrolysis products (*i.r.*). Crystals mounted in a sealed melting-point tube melted with decomposition at 192–194 °C.

A ground sample of $CH_3CSNSN^+AsF_6^-$ left exposed to a wet atmosphere for 1 h contained weak *i.r.* peaks attributable to NH_4^+ and sulphur–oxygen containing species. Pure $CH_3CSNSN^+AsF_6^-$ (in sulphur dioxide) gave a ¹H n.m.r. absorption at δ 4.82 p.p.m. (s, CH_3) (measured relative to $SiMe_4$, downfield direction positive) [Found: C, 7.75; N, 9.05; S, 20.80. $C_2H_3AsF_6N_2S_2$ requires C, 7.80; N, 9.10; S, 20.80%]. The *i.r.* and Raman spectra for $CH_3CSNSN^+AsF_6^-$ are reported in Table 1, and its mass spectrum in Table 2.

Preparation of $CH_3CSNSCH^+AsF_6^-$ (2). In a typical reaction CH_3CCH_3 (0.18 g, 4.50 mmol) was condensed onto S_2NaAsF_6 (1.07 g, 4.50 mmol) in liquid SO_2 (5.6 g). A straw-yellow solution was formed on warming to room temperature, which changed colour to burgundy and finally to a golden brown, after 6 h. SO_2Cl_2 (6.19 g) was added, giving a lower dark brown opaque layer under a clear upper layer. The two layers were separated into the two bulbs, and the solvent removed, giving an amorphous brown solid in one bulb, and small needle-like crystals in the other. The *i.r.* spectra of the brown solid (0.24 g) and the needles (0.93 g) were identical. The *i.r.* spectrum of the compound is given in Table 1, and the mass spectrum in Table 2. Crystals mounted in a sealed melting-point tube melted with decomposition at 195 °C. A ground sample exposed to moist air for 1–6 h showed a slow increase in hydrolysis products (NH_4^+ , SO) (*i.r.*). Pure $CH_3CSNSCH^+AsF_6^-$ (in sulphur dioxide) gave ¹H n.m.r. absorptions at δ 3.74 p.p.m. (s, CH_3) and 10.99 (s, H) (measured relative to $SiMe_4$, downfield direction positive) (Found: C, 11.65; H, 1.20; N, 4.55; S, 20.65. $C_3H_4AsF_6NS_2$ requires C, 11.70; H, 1.30; N, 4.55; S, 20.85%).

Preparation of $HCSNSCH^+AsF_6^-$ (3). In a typical reaction, C_2H_2 (0.13 g, 5.15 mmol) was condensed onto a solution of S_2NaAsF_6 (1.33 g, 5.00 mmol) in SO_2 (4.6 g). A straw coloured solution was obtained which became transparent and colourless after 1 h. SO_2Cl_2 (5.68 g) was added to the solution. The solvent was slowly condensed into the second bulb and small, distinct, needle-like crystals were obtained. The volatiles were removed giving a highly-crystalline colourless solid (1.47 g). The *i.r.* spectrum of the compound is given in Table 1, and the mass spectrum in Table 2. Crystals mounted in a sealed melting-point tube melted with decomposition at 216–217 °C. Pure $HCSNSCH^+AsF_6^-$ (in sulphur dioxide) gave a ¹H n.m.r. absorption at δ 12.10 p.p.m. (s, H) (measured relative to $SiMe_4$, downfield direction positive) (Found: C, 8.20; H, 0.70; N, 4.80; S, 21.85. $C_2H_2AsF_6NS_2$ requires C, 8.35; H, 0.40; N, 4.95; S, 21.75%).

Preparation of $CH_3CNSSN^+Cl^-$ (9).—(a) S_2Cl_2 (4.25 g, 31.5 mmol) in CH_3CN (20 cm³) was added dropwise over 2 h to a stirred slurry of NaN_3 (4.2 g, 64.6 mmol) in CH_3CN (40 cm³) at room temperature, and then heated for 6 h. After 1 h the initial purplish powder turned yellow. The mixture was stirred overnight, and filtered, giving a yellow powdery solid (6.2 g) containing S_4N_3Cl and N_3^- (*i.r.*), and a pale reddish brown solution. At $-20^\circ C$ the filtrate gave reddish crystals (50 mg) of $CH_3CNSSN^+Cl^-$, the *i.r.* data of which is given in Table 1 and mass spectra in Table 2. The melting point, with decomposition, was 185 °C (Found: C, 15.50; H, 1.50; Cl, 22.35; N, 17.00; S,

Table 1. Vibrational spectra (cm^{-1} , Nujol mulls for i.r.) of $\text{CH}_3\text{CSNSN}^+\text{AsF}_6^-$ (1), $\text{BrSCNSN}^+\text{Br}_3^-$ (8), $\text{CH}_3\text{CNSSN}^+\text{Cl}^-$ (9), $\text{CH}_3\text{CSNSCH}^+\text{AsF}_6^-$ (2), and $\text{HCSNSCH}^+\text{AsF}_6^-$ (3); Raman relative intensities are given in parentheses

(1) ^a		(8) ^b	(9) ^a	(2) ^a	(3) ^a	Some tentative assignments ^c
I.r. (mull)	Raman (solid)	I.r. (mull)	I.r. (mull)	I.r. (mull)	I.r. (mull)	
2 952w			2 930s 2 855mw 1 688w	3 088ms 2 920s 2 850m	3 090s	C-H str. CH ₃ str. ?
1 425 (sh) 1 409m	1 433vw?	1 334w 1 316vs	1 435m 1 405	1 463m		
1 368vw			1 397s 1 352m	1 391w		CH ₃ def. ?
1 154m 1 020w	1 154vw?	1 120vw	1 118w,br 1 030m 1 018w (sh) 992w	1 116m 1 066s 1 016vw 996w 960vw	1 267s	Asym. S-N str. CH ₃ rock
1 008vw 969vw 943vw	943(17)	970vs 922s	822s	888w 853vw 813ms 794ms	863s 827s 770s	C-C str. and/or ring vibration Ring vibrations
852ms 807ms	851(1) 804(36)	783vw 760vs 722m	860s 845vs	745vw		Sym. S-N str. and/or ring vibration Ring vibrations
696vs 681 (sh) 648m	693(3) 680(60) 649(14)	633s	632w 625w	696vs 677 (sh)	696s	ν_3 AsF ₆ ⁻ ν_1 AsF ₆ ⁻ Ring vibrations
595w	594(100)	572s 562m		612 (sh)	611 (sh)	C-S str.
577vw 563w	575(5)		543w 539m	579m 519ms 426mw		ν_2 AsF ₆ ⁻ Ring vibrations
447ms		414vs 394m			430 (sh)	S-Br str. and/or ring vibration
395s	370(12) 315(8)			394s	387s	ν_4 AsF ₆ ⁻ ν_5 AsF ₆ ⁻ ?

^a This work. ^b Ref. 6. ^c Tentative assignments were made by comparison of the above compounds, as well as AsF₆⁻ salts,²² H₂N-CSSC(NH₂)N⁺ salts,²³ CS₂ transition-metal complexes,³⁸ CH₃-C, C-N, and C-S bonds, and the relationship between $\nu_{\text{asym.}}$ and $\nu_{\text{sym.}}$ S-N stretches as by Banister²⁷ (see text).

41.05. C₂H₃ClN₂S₂ requires C, 15.50; H, 1.95; Cl, 23.00; N, 18.10; S, 41.45%.

(b) S₂Cl₂ (3.3 g, 24.4 mmol) in CH₃CN (30 cm³) was added dropwise over 2 h to a stirred slurry of LiN₃ (2.46 g, 50.2 mmol) in CH₃CN (50 cm³) at 0 °C. Evolution of N₂ and colour changes were immediate and in ca. 1 h the mixture was blue-black. After the addition of all the S₂Cl₂, the reaction mixture was stirred for 18 h at r.t. Initially, a purplish powdery solid was observed. N₂ evolution continued to nearly the end of the reaction. The final mixture was (i) a dark reddish brown thick oil, (ii) a pale pinkish powdery solid, and (iii) a yellow solution. They were separated by a careful decantation, followed by filtration.

The last traces of solvent were removed (10⁻³ Torr, 2 min) from (i) and weighed (1.7 g). Its i.r. spectrum showed two main peaks at 760 and 465 cm⁻¹. The intensity of the peak at 465 cm⁻¹ (probably S₂Cl₂) diminished on exposure to air. The oil was then sublimed at r.t. in vacuum (10⁻³ Torr) in a closed system into a liquid-nitrogen trap. In 4 h a small amount of

white crystalline material had deposited in the cold trap which on warming to r.t. suddenly turned black. The oily mass was sublimed for a further 2 h at 45, 60, and 75 °C, respectively. No more sublimate was collected. However, the oil had changed to a yellowish solid (1.59 g) which after washing with CS₂ (3 × 10 cm³), gave reasonably pure S₄N₃Cl (0.45 g).

The pale pink powdery solid product (ii) (2.2 g) appeared to be largely LiCl. The filtrate (iii) at -20 °C gave S₈ (50 mg) and a small amount of S₄N₃Cl. Removal of solvent gave a solid mixture of products (0.36 g) containing (9). No sulphur imides were detected.

X-Ray Structure Determination.—The crystals were subjected to a preliminary photographic investigation, to determine the space group and approximate alignment, and then mounted on a Picker FACS-I diffractometer equipped with graphite monochromated Mo-K_α radiation. In both cases cell parameters and orientation matrices were obtained by least squares using

Table 2. Mass spectra of $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ (1), $\text{CH}_3\overline{\text{CNSSN}}^+\text{Cl}^-$ (9), $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ (2), and $\overline{\text{HCSNSCH}}^+\text{AsF}_6^-$ (3)

<i>m/e</i>	Ion	Intensity (%)			
		(1) ^a	(9) ^b	(2) ^c	(3) ^c
151	AsF_5^+	4		12	20
132	AsF_3^+	11		63	37
123	$(\text{CH}_3\text{CN})_3^+$	>100			
119	$\text{CH}_3\text{CS}_2\text{N}_2$	8	62		
118	$\text{C}_3\text{H}_4\text{S}_2\text{N}$			13	
113	AsF_2^+	13		100	100
105	$\text{CH}_3\text{CS}_2\text{N}^+$	6			
104	$\text{C}_3\text{H}_4\text{S}_2^+$			2	4
103	$\text{C}_3\text{H}_3\text{S}_2^+$ or $\text{C}_2\text{HS}_2\text{N}^+$			15	
94	AsF^+			7	12
82	$(\text{CH}_3\text{CN})_2^+$	>100			
78	S_2N^+	18	100	19	25
76	CS_2^+		21		8
75	As^+			4	14
73	CH_3CNS^+	66	56		<1
64	S_2^+	25	24	9	11
59	CH_3CS^+	8		39	<1
58	SCN^+ or CH_2CS^+			4	4
47	HSN^+ or CH_3S^+		37	6	8
46	SN^+	16	39	6	13
45	HCS^+	12	17	9	14
44	CS^+	17	26	6	10
41	CH_3CN^+	100	42		<1
40	CH_2CN^+		34		
38	H^{37}Cl^+		30		
37	$^{37}\text{Cl}^+$		4		
36	H^{35}Cl^+		86		
35	$^{35}\text{Cl}^+$		13		
32	S^+	23		5	14
27	CH_3C^+	11		2	

^a 110 °C, 70 eV, direct inlet; sample contains a small amount of the more volatile species 2,4,6-trimethyl-1,3,5-triazine (*i.e.* peaks at *m/e* = 123, 82, and 41). ^b 110 °C, 70 eV, direct inlet. ^c 140 °C, 70 eV, direct inlet.

Table 3. Crystal data for $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ (1) and $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ (2)

	(1)	(2)
Formula	$\text{C}_2\text{H}_3\text{AsF}_6\text{N}_2\text{S}_2$	$\text{C}_3\text{H}_4\text{AsF}_6\text{NS}_2$
<i>M</i>	308.9	307.10
System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
<i>a</i> /Å	8.182(7)	8.539(5)
<i>b</i> /Å	9.822(3)	9.941(2)
<i>c</i> /Å	11.515(7)	12.053(5)
β /°	110.91(6)	116.69(4)
<i>U</i> /Å ³	864	914
<i>Z</i>	4	4
<i>D_c</i> /g cm ⁻³	2.37	2.23
Crystal size/mm	0.25 × 0.30 × 0.40	0.30 × 0.30 × 0.39
μ /mm ⁻¹	4.44	4.19
<i>F</i> (000)	592	592
$\sin 2\theta_{\text{max}}$	45	45
λ /Å	0.710 69	0.710 69
Temp./K	100	298
No. unique reflections	1 391	1 612
No. observed [<i>I</i> > 2σ(<i>I</i>)]	893	1 077
<i>R</i> (= Σ Δ <i>F</i> /Σ <i>F</i>)	0.12	0.049
<i>R'</i> (= Σ <i>w</i> Δ <i>F</i> ² /Σ <i>w</i> <i>F</i> ²)	0.14	0.057

the co-ordinates of 12 Friedel pairs of centred reflections in the range $30 \leq 2\theta \leq 45^\circ$. Intensity data were collected using an ω - 2θ scan of $2^\circ (2\theta) \text{ min}^{-1}$. Background intensities were estimated from a standing count at each end of the scans and if a peak was considered significant [$I \geq 2\sigma(I)$] an analysis of the peak profile was performed. The diffractometer was controlled by a

PDP8/A computer running the FORTRAN program of Larson and Gabe.¹⁶ In the case of $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ an Enraf-Nonius low-temperature system was used to pass a stream of cold N_2 over the crystal.

After data reduction the crystal structures were solved using the MULTAN-80 suite of direct-method programs.¹⁷

Table 4. Fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ (1)

Atom	X/a	Y/b	Z/c
S(1)	0.187 8(9)	0.698 7(4)	0.234 2(5)
S(2)	0.262 0(7)	0.926 8(5)	0.364 0(4)
N(1)	0.269(3)	0.802(2)	0.451(2)
N(2)	0.207(2)	0.864(2)	0.229(1)
C(1)	0.243(3)	0.681(2)	0.397(2)
C(2)	0.245(3)	0.549(2)	0.455(2)
H(1)	0.2871	0.4760	0.4100
H(2)	0.1036	0.5556	0.4176
H(3)	0.2886	0.5308	0.5535
As(1)*	0.738 9(3)	0.7977(2)	0.346 9(2)
F(1)	0.879(2)	0.903(1)	0.313(1)
F(2)	0.591(3)	0.829(2)	0.203(1)
F(3)	0.594(2)	0.694(1)	0.374(2)
F(4)	0.815(2)	0.667(2)	0.292(2)
F(5)	0.662(3)	0.928(2)	0.407(2)
F(6)	0.889(3)	0.770(3)	0.491(2)
F(11)	0.6120	0.8136	0.4335
F(21)	0.8660	0.7837	0.2606
F(31)	0.8030	0.9609	0.3789
F(41)	0.6751	0.6352	0.3148
F(51)	0.9065	0.7468	0.4733
F(61)	0.5710	0.8496	0.2208

* Atoms F(1)—F(6) were included with 90% occupancy, F(11)—F(16) were constrained to retain octahedral geometry and given 10% occupancy.

An initial attempt to refine a room temperature data set for $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ failed, resulting in extremely high thermal parameters for some of the light atoms and residuals of ca. 0.20. The data were recollected at low temperature with somewhat better results. The structures were refined by least-squares techniques with all atoms allowed to vary anisotropically. Hydrogen atoms were included in the final cycles with fixed calculated positions and thermal parameters. In both structures after the refinement had converged the fluorine thermal parameters were abnormally large and difference syntheses showed peaks between these atomic positions. In an attempt to accommodate this feature, the AsF_6^- units were each represented by two units with their As positions constrained to be equal. In the case of $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ these units had occupancies of 0.6 and 0.4 and resulted in a significant improvement in the final *R* from 0.062 to 0.049. For $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ the occupancy of the minor unit was only 0.1, resulting in no improvement in the fit of the model.

Scattering factors were taken from ref. 18 and those for sulphur and arsenic were corrected for anomalous dispersion. Crystal data are given in Table 3. Final atomic co-ordinates are given in Tables 4 and 5. Calculations were carried out on the PDP8/A computer using the programs of Larson and Gabe,¹⁶ and on a Wicat Systems 150-WS using SHELX-76.¹⁹

Radical Preparation.—Radicals were prepared by the addition of silver powder to acetonitrile solutions of the AsF_6^- salts of (1), (2), and (3). However, the most efficient method is to dissolve ca. 5 mg of the salt in 1 cm³ of tetrahydrofuran (freshly distilled from the benzophenone anion radical) and then to add ca. 20 mg of sodium dithionite. The radical takes several minutes to form at room temperature. The solutions were then subjected to several freeze-pump-thaw cycles to remove oxygen. Different solvents could be used by pumping off the tetrahydrofuran after radical production and then introducing the desired solvent.

Table 5. Fractional atomic co-ordinates with e.s.d.s in parentheses for $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ (2)

Atom	X/a	Y/b	Z/c
S(1)	0.854 4(3)	0.299 9(2)	0.249 3(2)
S(2)	0.748 6(3)	0.063 0(2)	0.138 7(2)
N(1)	0.839 9(9)	0.140 5(7)	0.267 5(6)
C(1)	0.707 9(10)	0.189 1(8)	0.037 8(7)
C(2)	0.762 6(9)	0.314 8(7)	0.094 1(6)
C(3)	7.527(11)	0.442 8(7)	0.031 4(8)
H(1)	0.6647	0.1417	-0.0546
H(3A)	0.6664	0.4274	-0.0701
H(3B)	0.8756	0.4849	0.0410
H(3C)	0.6892	0.5183	0.0634
As(1)*	0.276 0(1)	0.193 6(1)	0.151 8(1)
F(1)	0.183 5(12)	0.339 7(7)	0.162 8(10)
F(2)	0.369 5(12)	0.048 8(7)	0.137 8(11)
F(3)	0.100(3)	0.190(4)	0.018(2)
F(4)	0.445(3)	0.204(4)	0.282(2)
F(5)	0.164(3)	0.113(2)	0.209(3)
F(6)	0.396(3)	0.279(2)	0.098(3)
F(11)	0.453(3)	0.282(2)	0.204(3)
F(12)	0.351(6)	0.180(4)	0.306(2)
F(13)	0.235(7)	0.210(3)	0.011(2)
F(14)	0.107(4)	0.090(3)	0.112(5)

* The anion was refined as two octahedra with a common F(1)—As(1)—F(2) axis, thus F(1) and F(2) were given 100% occupancy, F(3)—F(6) 58%, and F(11)—F(14) 42%.

The deuteriated 5-methyl-1,3,2,4-dithiadiazolium salt was prepared by adding [²H₃]acetonitrile (0.5 g, 99 atom %) (Merck, Sharp, and Dohme, Canada, Ltd.) to dithianitronium hexafluoroarsenate (0.1 g): after leaving the mixture overnight at room temperature the excess acetonitrile was pumped off. The radical from this salt was dissolved in 99.6 atom % perdeuteriotoluene (Merck, Sharp, and Dohme).

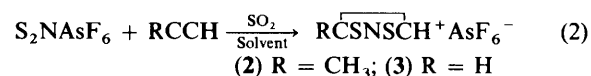
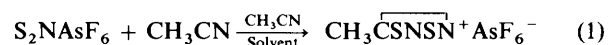
E.S.R. Measurements.—A Varian E-4 X-band e.s.r. spectrometer was used to obtain the spectra. Details of spectrometer calibration, *g*-factor measurements, and computer simulations have been given previously.^{20,21}

Cyclic Voltammetry.—Experiments were conducted at 20 °C using a conventional potentiostat having platinum working and auxiliary electrodes, and a reference electrode of Ag—Ag⁺ (0.01 mol dm⁻³ in acetonitrile containing 0.1 mol dm⁻³ tetrabutylammonium tetrafluoroborate).

Solutions of the substrate salts (5 mmol dm⁻³) in acetonitrile containing 0.1 mol dm⁻³ tetrabutylammonium tetrafluoroborate, as supporting electrolyte, were purged with nitrogen and scanned at 400 mV s⁻¹: the voltammogram was recorded with a Watanabe XY recorder.

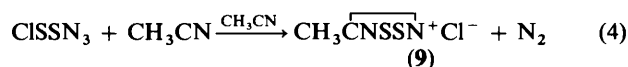
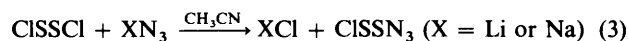
Results and Discussion

Preparation and Characterisation of $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ (1), $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ (2), $\text{HCSNSCH}^+\text{AsF}_6^-$ (3), and $\text{CH}_3\overline{\text{CNSSN}}^+\text{Cl}^-$ (9).—The AsF_6^- salts of (1), (2), and (3) were prepared essentially quantitatively at room temperature according to equations (1) and (2). Presumably the reactions are symmetry-allowed concerted additions of the π electrons from



the highest occupied molecular orbitals (h.o.m.o.) of the respective triple bonds of HCCR and CH₃CN to the lowest unoccupied molecular orbital (l.u.m.o.) of S₂N⁺. It is likely that these reactions are general and that a range of derivatives of the cationic heterocycles can be similarly prepared.

We also prepared the disulphide isomer of (1), CH₃CNSSN⁺Cl⁻ (9), in low yield by the reaction of S₂Cl₂ with NaN₃ or LiN₃ in CH₃CN. These reactions may proceed by equations (3) and (4). In the reaction using LiN₃, a volatile product, likely to be



S₂N₂, was isolated, and which polymerized to a black solid which was probably poly(sulphur nitride). The S₂N₂ was

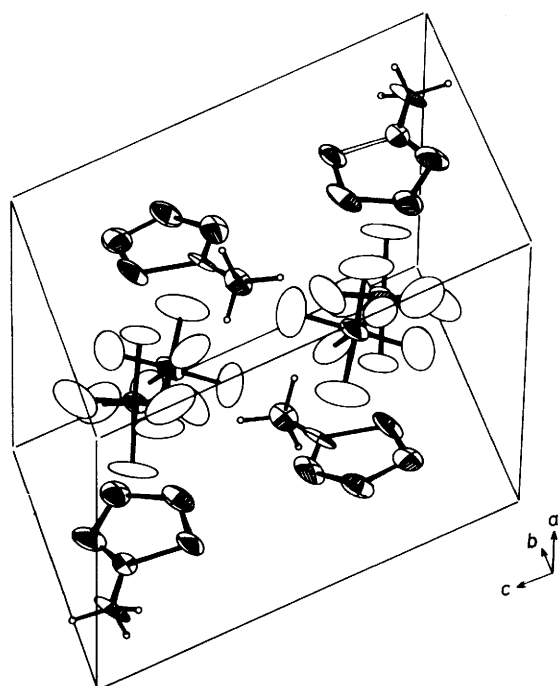


Figure 1. Contents of unit cell of CH₃CSNSN⁺AsF₆⁻ (1)

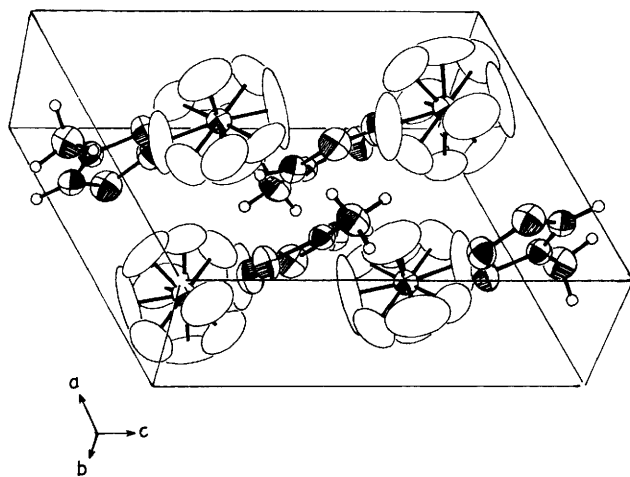


Figure 2. Contents of unit cell of CH₃CSNSCH⁺AsF₆⁻ (2)

probably formed by further reaction of ClSSN₃ with LiN₃. CH₃CNSSN⁺Cl⁻ (9) was also formed in low yields in a variety of related reactions in acetonitrile that gave poly(sulphur nitride) as the major product,⁷ and by the reaction of NH₄Cl and SCl₂ in acetonitrile.⁸

The identity of all four compounds is supported by their elemental analysis, vibrational spectra (Table 1), and mass spectra (Table 2). The i.r. spectrum of the analogous cation BrSCNSN⁺Br₃⁻ (8)⁶ is compared to those of CH₃CSNSN⁺AsF₆⁻ (1), CH₃CNSSN⁺Cl⁻ (9), CH₃CSNSCH⁺AsF₆⁻ (2), and HCSNSCH⁺AsF₆⁻ (3) in Table 1. The vibrational spectra of (1), (2), and (3) are consistent with the presence of AsF₆⁻,²² a C-S bond²³ [$\nu(\text{C-S})$ at 595 in (1), 612 in (2), 611 in (3), and 572 or 562 cm⁻¹ in (8)], and a methyl group in the case of (1) and (2).

The mass spectra of the AsF₆⁻ salts of (1), (2), and (3) were all attributable to ions derived from the neutral species produced on dissociation according to equation (5). The neutral fluorides

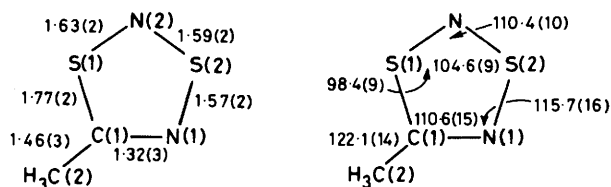
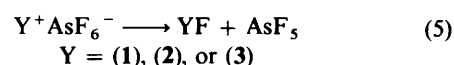


Figure 3. Bond distances (Å) and angles (°) in CH₃CSNSN⁺ (1)

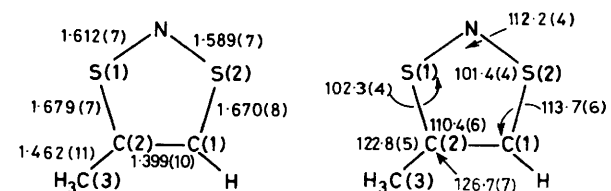


Figure 4. Bond distances (Å) and angles (°) in CH₃CSNSCH⁺ (2)

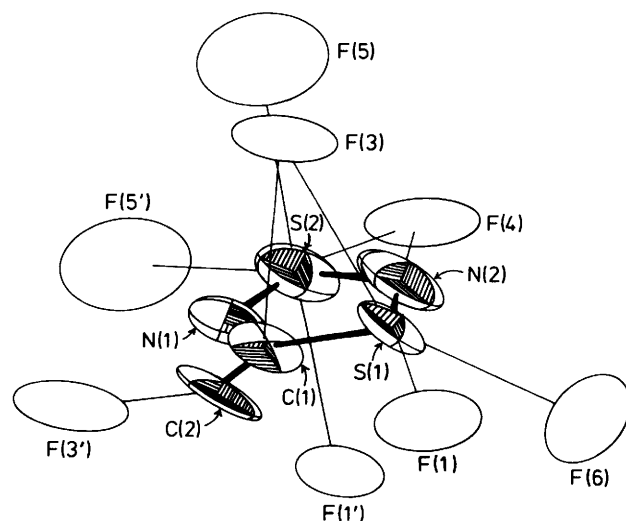


Figure 5. Cation-anion interactions in CH₃CSNSN⁺AsF₆⁻ (1); the fluorine atoms assigned to the AsF₆⁻ of 10% occupancy are not included

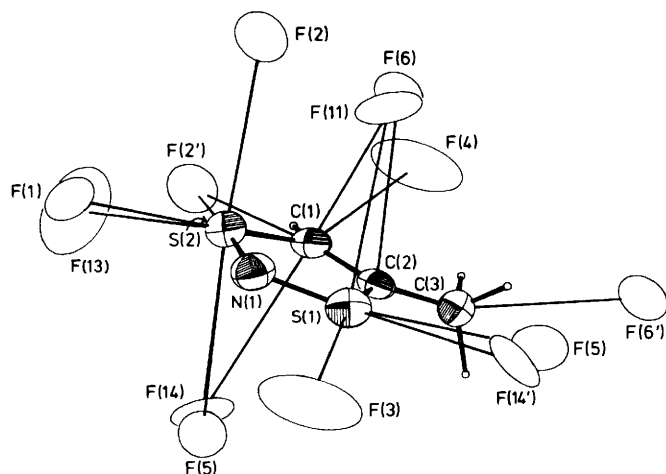


Figure 6. Cation-anion interactions in $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ (2); the fluorine atoms assigned to the AsF_6^- of 40% are occupancy are denoted by two-digit numbers

Table 6. Bond distances (Å) and angles (°) for $\text{CH}_3\overline{\text{CSNSN}}^+$ (1) including interionic contacts, with e.s.d.s in parentheses

(a) $\text{CH}_3\overline{\text{CSNSN}}^+$			
S(1)-C(1)	1.77(2)	C(1)-S(1)-N(2)	98.4(9)
S(1)-N(2)	1.63(2)	S(1)-N(1)-S(2)	110.4(1.0)
N(2)-S(2)	1.59(2)	N(2)-S(2)-N(1)	104.6(9)
S(2)-N(1)	1.57(2)	S(2)-N(1)-C(1)	115.7(1.6)
N(1)-C(1)	1.32(3)	N(1)-C(1)-S(1)	110.6(1.5)
C(1)-C(2)	1.46(3) ^a	N(1)-C(1)-C(2)	127.2(1.9)
		S(1)-C(1)-C(2)	122.1(1.4)
(b) Interionic contacts ^{b,c}			
S(1)-F(1)	2.97(2)	F(1)-S(1)-N(2)	168.1(8)
S(1)-F(3)	3.13(2)	F(3)-S(1)-N(2)	86.5(7)
S(1)-F(6)	3.01(2)	F(3)-S(1)-C(1)	68.5(9)
S(2)-F(1)	2.98(2)	F(6)-S(1)-C(1)	144.2(9)
S(2)-F(4)	2.89(2)	F(6)-S(1)-N(2)	85.2(8)
S(2)-F(5)	3.13(2)	F(1')-S(2)-N(1)	82.2(8)
S(2)-F(5')	2.87(2)	F(1')-S(2)-N(2)	82.1(8)
N(1)-F(5')	3.07(2)	F(4)-S(2)-N(1)	169.2(8)
N(2)-F(4)	2.99(2)	F(5)-S(2)-N(1)	95.9(9)
C(1)-F(3)	2.98(3)	F(5)-S(2)-N(2)	94.2(9)
C(2)-F(1)	3.22(3)	F(5)-S(2)-N(2)	172.6(8)
C(2)-F(3')	3.08(3)	F(5')-N(1)-C(1)	176.5(9)
		F(4)-N(2)-S(1)	171.8(7)
		F(3)-C(1)-S(1)	78.0(1.0)
		F(3)-C(1)-N(1)	90.3(1.5)
		F(3)-C(1)-C(2)	103.1(1.5)
		F(1)-C(2)-C(1)	90.5(1.5)
		F(3')-C(2)-C(1)	156.4(1.5)

^a Although this bond appears short, libration correction with C(2) riding on C(1) indicates a bond length of 1.50 Å. ^b All contacts included for $\text{S}\cdots\text{F} \leq 3.30$, $\text{C}\cdots\text{F} \leq 3.22$, and $\text{N}\cdots\text{F} \leq 3.07$ Å. Van der Waals radii: $\text{S}\cdots\text{F} = 3.27$, $\text{C}\cdots\text{F} = 3.17$, and $\text{N}\cdots\text{F} = 3.02$ Å.³¹ ^c Selected interionic contact angles given.

are not detectable in the mass spectra, but ions derived from them (e.g. AsF_4^+ and Y^+ and derived fragments) are observed. It is noted that the fragment CH_3CS^+ , $m/e = 59$, is present in the spectra of (1), (2), and (3), but not in $\text{CH}_3\overline{\text{CNSSN}}^+\text{Cl}^-$ (9), which does not contain a carbon-sulphur bond.

X-Ray Crystal Structures of $\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ (1) and $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ (2).—The contents of the unit cells of

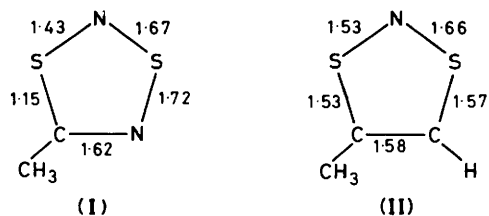


Table 7. Bond distances (Å) and angles (°) for $\text{CH}_3\overline{\text{CSNSCH}}^+$ (2) including interionic contacts, with e.s.d.s in parentheses

(a) $\text{CH}_3\overline{\text{CSNSCH}}^+$			
C(1)-C(2)	1.399(10)	N(1)-S(1)-C(2)	102.3(4)
C(2)-C(3) ^a	1.462(11)	N(1)-S(2)-C(1)	101.4(4)
C(2)-S(1)	1.679(7)	S(2)-N(1)-S(1)	112.2(4)
S(1)-N(1)	1.612(7)	C(2)-C(1)-S(2)	113.7(6)
N(1)-S(2)	1.589(7)	C(1)-C(2)-C(3)	126.7(7)
S(2)-C(1)	1.670(8)	C(1)-C(2)-S(1)	110.4(6)
		C(3)-C(2)-S(1)	122.8(5)
(b) Interionic contacts ^{b,c}			
S(1)-F(3)	2.96(4)	N(1)-S(1)-F(3)	86.9(7)
S(1)-F(5)	3.16(4)	N(1)-S(1)-F(5)	158.7(6)
S(1)-F(11)	3.23(4)	N(1)-S(1)-F(11)	80.1(5)
S(1)-F(14')	3.27(5)	N(1)-S(1)-F(14')	142.4(7)
S(2)-F(1)	3.12(1)	C(2)-S(1)-F(3)	163.8(7)
S(2)-F(2')	3.21(1)	C(2)-S(1)-F(5)	93.3(6)
S(2)-F(14)	3.22(5)	C(2)-S(1)-F(11)	83.6(7)
S(2)-F(2)	3.24(1)	C(2)-S(1)-F(14)	112.4(7)
S(2)-F(5)	3.29(4)	N(1)-S(2)-F(2')	165.5(4)
S(2)-F(13)	3.29(7)	N(2)-S(2)-F(14)	89.3(7)
C(1)-F(2)	3.04(2)	N(1)-S(2)-F(2)	94.3(4)
C(1)-F(4)	3.07(5)	N(1)-S(2)-F(5)	71.2(6)
C(1)-F(6)	3.18(4)	N(1)-S(2)-F(1)	75.8(4)
C(2)-F(6)	3.17(3)	N(1)-S(2)-F(13)	144.3(10)
C(3)-F(6')	3.15(3)	C(1)-S(2)-F(2')	68.8(4)
S(2)-C(1)-F(2')	80.4(4)	C(1)-S(2)-F(14)	76.2(8)
S(2)-C(1)-F(4)	143.9(8)	C(1)-S(2)-F(2)	98.6(4)
S(2)-C(1)-F(6)	88.0(6)	C(1)-S(2)-F(5)	85.6(6)
C(2)-C(1)-F(2')	162.4(7)	C(1)-S(2)-F(1)	176.3(4)
C(2)-C(1)-F(4)	96.5(8)	C(1)-S(2)-F(13)	105.3(9)
C(2)-C(1)-F(6)	76.7(7)		
C(1)-C(2)-F(6)	77.9(7)		
S(1)-C(2)-F(6)	86.7(5)		
C(2)-C(3)-F(6')	159.6(8)		

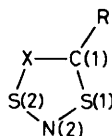
^a Although this bond appears short, libration correction with C(3) riding on C(2) indicates a bond length of 1.522 Å. ^b All contacts included for $\text{S}\cdots\text{F} \leq 3.30$, $\text{C}\cdots\text{F} \leq 3.22$, and $\text{N}\cdots\text{F} \leq 3.07$ Å. Van der Waals radii: $\text{S}\cdots\text{F} = 3.27$, $\text{C}\cdots\text{F} = 3.17$, and $\text{N}\cdots\text{F} = 3.02$ Å.³¹ ^c Selected interionic contact angles given.

$\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ (1) and $\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ (2) are shown in Figures 1 and 2 respectively. The bond distances and angles within each of the cations (1) and (2) are given in Figures 3 and 4. Figures 5 and 6 show the cations and their cation-anion contacts. Bond distances and angles not given in Figures 3 and 4 are given in Tables 6 and 7.

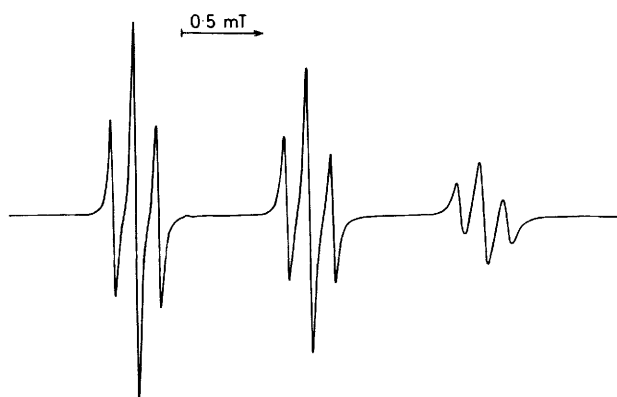
The bond lengths in various $\overline{\text{RCSNSX}}$ ($\text{X} = \text{C}$ or N) containing compounds are compared in Table 8. All the $\overline{\text{CSNSN}}$ and $\overline{\text{CSNSC}}$ rings are planar, and the bond distances and angles, where available, are similar whether the molecules are neutral or cationic. However, small differences between related rings are discernible. The C-S and C-N bonds adjacent to C-R are longer the greater the π -donor strength of R. Similar behaviour is observed for derivatives of S_3N_2 rings.²⁴⁻²⁶ The average NSN angles in (1) and (2), and in the related species

Table 8. Bond distances (Å) about rings that are related to $\text{CH}_3\overline{\text{CSNSN}}^+$ (1) and $\text{CH}_3\overline{\text{CSNSCH}}^+$ (2)

Compound	S(1)-N(2)	N(2)-S(2)	S(2)-X	X-C(1)	C(1)-S(1)	C(1)-R
$\text{CH}_3\overline{\text{CSNSN}}^+\text{AsF}_6^-$ (1) ^a	1.63(2)	1.59(2)	1.57(2)	1.32(3)	1.77(2)	1.46(3)
$\text{BrSCNSN}^+\text{Br}_3^-$ ^b	1.67(1)	1.56(2)	1.60(2)	1.37(2)	1.76(1)	1.72(1)
$\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{O})\overline{\text{NCSNSN}}^c$	1.659(4)	1.555(4)	1.580(4)	1.351(5)	1.788(5)	1.303(5)
OCSNSNAsF_5^d	1.602(7)	1.566(1)	1.585(5)	1.323(4)	1.757(2)	1.279(4)
$[\text{Zn}(\text{OCSNSN})_6]^{2+}[\text{AsF}_6]^{-2e}$	1.617(2)	1.570(3)	1.576(3)	1.347(3)	1.789(3)	1.240(3)
OCSNSN^f	1.629(5)	1.572(6)	1.584(5)	1.375(10)	1.813(7)	1.219(7)
$\text{CH}_3\overline{\text{CSNSCH}}^+\text{AsF}_6^-$ (2) ^g	1.612(7)	1.589(7)	1.670(8)	1.399(10)	1.679(7)	1.462(11)
$\text{C}_6\text{H}_5(\text{N}_2\text{C}_2\text{S})\overline{\text{NCSNSC}}\text{C}_6\text{H}_5^h$	1.609(9)	1.568(9)	1.768(9)	1.437(12)	1.673(8)	—



^a X = N(1), R = $\text{H}_3\text{C}(2)$. ^b Ref. 6; X = N(1), R = BrS(3). ^c Ref. 40, X = N, R = $\text{NC}(\text{O})\text{C}_6\text{H}_4\text{CH}_3$. ^d Ref. 25; X = N, R = O-AsF₅. ^e Ref. 26; X = N, R = O-Zn^{II}(OCSNSN)₅. ^f Ref. 24; X = N, R = O, average bond distances of the two OCSNSN molecules found in the asymmetric unit cell are reported here. ^g X = HC(1), R = $\text{H}_3\text{C}(3)$. ^h Ref. 3; X = $\text{C}_6\text{H}_5(\text{N}_2\text{C}_2\text{S})\text{NC}(1)$, R = C_6H_5 .

**Figure 7.** First-derivative X-band e.s.r. spectrum at -114.0°C of the 1,3,2-dithiazol-2-yl radical in thf

given in Table 8, fit Banister's relationship²⁷ between average N-S bond distances and NSN angles for an unstrained rather than a strained system.

Compounds (1), (2), and (9) can be regarded as 6π aromatic rings.²⁸ Bond orders (b.o.) can be estimated using Nyberg's equation, [(6); $d(\text{NS}) = \text{N-S distance in Å}$]²⁹ and Pauling's equation, (7),³⁰ and are given in (I) and (II); D_n is the sum of the

$$\text{b.o.}(\text{NS}) = 0.429 + 6.850d(\text{NS}) + 3.825d(\text{NS})^2 \quad (6)$$

$$D_n = D_1 - 0.71 \log(\text{b.o.}) \quad (7)$$

appropriate covalent radii (Å) and D_1 for C-C = 1.54, for C-N = 1.47, and for C-S = 1.81 Å.³¹

The standard deviations are high for the bond lengths in (1), therefore the bond orders in (I) are uncertain. It is clear, however, that there is extensive delocalisation in (II) and probably extensive delocalisation in (I).

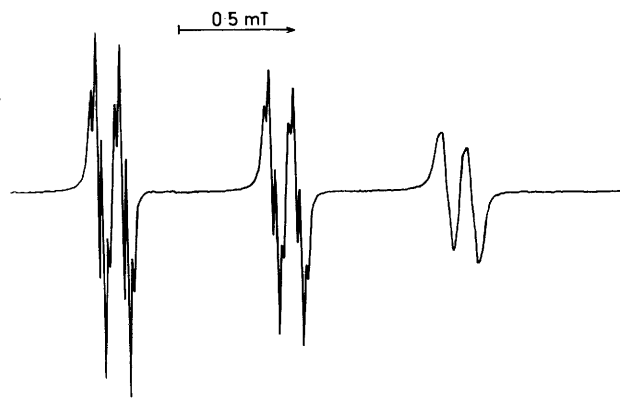
The anionic fluorine contacts with both the $\text{CH}_3\overline{\text{CSNSN}}^+$ and $\text{CH}_3\overline{\text{CSNSCH}}^+$ cations are shown in Figures 5 and 6 respectively. These contacts are either in the plane or at 90° ($\pm 20^\circ$) to the rings.³² The contacts are to the carbon and

Table 9. Hyperfine coupling constants^a and linewidths^{a,b} of the 1,3,2-dithiazol-2-yl radical in toluene

Temp./°C	a^N/mT	a^H/mT	Linewidth/mT
+20.2	1.071 ± 0.001	0.134 ± 0.009	0.072 ± 0.001
-56.8	1.061 ± 0.001	0.136 ± 0.001	0.0493 ± 0.0005
-70.8	1.056 ± 0.001	0.133 ± 0.002	0.0330 ± 0.0004
-85.6	1.055 ± 0.003	0.136 ± 0.002	0.0265 ± 0.0003
-97.9	1.053 ± 0.003	0.135 ± 0.002	0.0280 ± 0.0003
-108.5	1.045 ± 0.001	0.137 ± 0.002	0.0534 ± 0.0006

$da^N/dT = +3.0 \times 10^{-4} \text{ mT K}^{-1}$, $da^H/dT \sim 0$, $g \text{ factor} = 2.00692$ (tetrahydrofuran at -37.5°C)

^a Error limits are one standard deviation. ^b Central line of low-field triplet.

**Figure 8.** First-derivative X-band e.s.r. spectrum at -110.2°C of the 4-methyl-1,3,2-dithiazol-2-yl radical in thf

sulphur atoms of each ring, contacts to the nitrogen atoms are essentially at the appropriate sum of the van der Waal's radii (see Table 6). This implies that the positive charge is delocalised between the carbon and nitrogen atoms in the ring.

The geometry about the AsF_6^- anions is that of a distorted octahedron, but due to high standard deviations in the fluorine positions, no significant correlation can be made between the

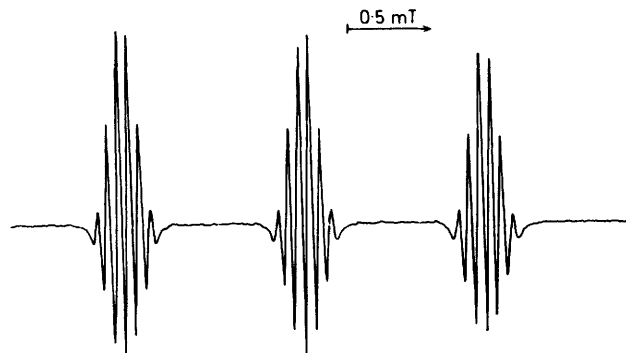


Figure 9. Second-derivative X-band e.s.r. spectrum at -51.9°C of the 5-methyl-1,3,2-dithiadiazol-2-yl radical in acetonitrile

lengths of the As-F bonds and the strength or number of contacts which the fluorine atoms make with the cations.

E.S.R. Spectra.—For optimum resolution two conditions had to be fulfilled: (i) the concentration of the unreduced 1,3,2-dithiazolium or 1,3,2,4-dithiadiazolium salt had to be kept low, or destroyed completely with an alkali-metal chloride, in order to minimize broadening from electron exchange, and (ii) the temperature had to be below ambient in order to reduce broadening from out-of-plane vibrations about the sulphur-sulphur axis¹⁴ and from spin rotational relaxation which occurs in small, rapidly tumbling radicals. The spectra shown in Figures 7–9 were obtained under these conditions. Spectra were recorded over a wide range of temperatures that enabled the temperature coefficients of the hyperfine coupling constants to be determined (see Tables 9–11). From Figures 7–9, the small size of the radical is evident from the relatively small effect of

Table 10. Hyperfine coupling constants^a and linewidths^{a,b} of the 4-methyl-1,3,2-dithiazol-2-yl radical in toluene and in tetrahydrofuran (thf)

Solvent	Temp./ $^{\circ}\text{C}$	a^{N}/mT	$a_{\text{H}}^{\text{H}}/\text{mT}$	$a_{\text{CH}_3}^{\text{H}}/\text{mT}$	Linewidth/mT
Toluene	+20.3	1.065 ± 0.003	0.150 ± 0.001	—	0.0738 ± 0.0007
	+2.0	1.061 ± 0.001	0.153 ± 0.001	—	0.0705 ± 0.0003
	-15.7	1.059 ± 0.001	0.153 ± 0.001	—	0.0662 ± 0.0004
	-51.8	1.061 ± 0.001	0.149 ± 0.002	—	0.0518 ± 0.0006
	-68.7	1.053 ± 0.003	0.153 ± 0.001	0.0260 ± 0.0034	0.0173 ± 0.0002
	-94.3	1.051 ± 0.003	0.157 ± 0.001	0.0286 ± 0.0007	0.0191 ± 0.0008
$da^{\text{N}}/dT = +1.2 \times 10^{-4} \text{ mT K}^{-1}$, $da_{\text{H}}^{\text{H}}/dT = -1.5 \times 10^{-4} \text{ mT K}^{-1}$, $da_{\text{CH}_3}^{\text{H}}/dT = -1.0 \times 10^{-4} \text{ mT K}^{-1}$					
thf	-22.7	1.065 ± 0.003	0.136 ± 0.009	—	0.089 ± 0.010
	+3.1	1.064 ± 0.001	0.138 ± 0.005	—	0.079 ± 0.005
	-11.4	1.060 ± 0.003	0.139 ± 0.003	—	0.070 ± 0.003
	-31.5	1.059 ± 0.001	0.1454 ± 0.0005	—	0.069 ± 0.001
	-44.1	1.056 ± 0.002	0.1492 ± 0.004	—	0.069 ± 0.001
	-61.0	1.054 ± 0.002	0.1497 ± 0.0005	—	0.038 ± 0.002
	-86.2	1.049 ± 0.003	0.1539 ± 0.0007	0.0306 ± 0.0003	0.0193 ± 0.0006
	-110.2	1.047 ± 0.001	0.1564 ± 0.0002	0.0332 ± 0.0009	0.0180 ± 0.0006
$da^{\text{N}}/dT = +1.1 \times 10^{-4} \text{ mT K}^{-1}$, $da_{\text{H}}^{\text{H}}/dT = -1.0 \times 10^{-4} \text{ mT K}^{-1}$, $da_{\text{CH}_3}^{\text{H}}/dT = -1.1 \times 10^{-4} \text{ mT K}^{-1}$					

^a Error limits are one standard deviation. ^b Low-field signal.

Table 11. Hyperfine coupling constants^a and linewidths^{a,b} of the 5-methyl-1,3,2,4-dithiadiazol-2-yl radical in acetonitrile, thf, and [²H₈]toluene

Solvent	Temp./ $^{\circ}\text{C}$	$a^{\text{N}(2)}/\text{mT}$	$a^{\text{N}(4)} = a_{\text{CH}_3}^{\text{H}}/\text{mT}$	Linewidth/mT
Acetonitrile	+10.8	1.108 ± 0.005	—	0.120
	-9.5	1.101 ± 0.001	—	0.118
	-41.6	1.097 ± 0.003	0.062 ± 0.002	0.051
	-51.9	1.095 ± 0.001	0.064 ± 0.001	0.0305
	-65.1	1.086 ± 0.003	0.066 ± 0.002	0.029
$da^{\text{N}(2)}/dT = +2.9 \times 10^{-4} \text{ mT K}^{-1}$, $da^{\text{N}(4)}/dT = -2 \times 10^{-4} \text{ mT K}^{-1}$				
thf	+23.4	1.106 ± 0.002	—	0.21
	-6.9	1.104 ± 0.002	—	0.20
	-34.3	1.110 ± 0.005	0.061 ± 0.006	0.040 ± 0.008
	-51.5	1.101 ± 0.001	0.063 ± 0.003	0.032 ± 0.003
	-68.3	1.099 ± 0.002	0.061 ± 0.001	0.027 ± 0.001
	-85.4	1.099 ± 0.003	$0.062 \pm 0.002^{\text{c}}$	0.026 ± 0.001
	-101.1	1.100 ± 0.002	$0.063 \pm 0.002^{\text{d}}$	0.024 ± 0.002
$da^{\text{N}(2)}/dT = +6 \times 10^{-5} \text{ mT K}^{-1}$, $da^{\text{N}(4)}/dT = -6 \times 10^{-5} \text{ mT K}^{-1}$				
[² H ₈]toluene ^e	+22.0	1.101 ± 0.002	$0.0578 \pm 0.0015^{\text{f}}$	0.024 ± 0.001
	-39.0	1.101 ± 0.004	$0.0439 \pm 0.0010^{\text{f}}$	0.023 ± 0.001

g factor = 2.00532 ± 0.00005 (toluene)

^a Error limits are one standard deviation. ^b Low-field group. ^c $a^{\text{N}(4)}$ and $a_{\text{CH}_3}^{\text{H}}$ estimated to be 0.0647 ± 0.0010 and 0.0613 ± 0.0003 mT respectively. ^d $a^{\text{N}(4)}$ and $a_{\text{CH}_3}^{\text{H}}$ estimated to be 0.0657 ± 0.0014 and 0.0609 ± 0.0005 mT respectively. ^e Data are for the perdeuterated radical. ^f $a^{\text{N}(4)}$.

asymmetric line broadening. Indeed, they are probably the smallest radicals yet discovered that are stable in solution at room temperature; because of this property and also their rigidity and lack of polarity, they make excellent models for spin probes.³³ Tables 9–11 show that the values of $a^{N(2)}$ are virtually independent of the substituents and solvent, even when the CH group is replaced by a nitrogen atom in the heterocyclic ring. The near equality of $a^{N(4)}$ and $a_{CH_3}^H$ for the radical (11) led us to prepare a fully deuterated version of this radical; the e.s.r. spectrum comprised a simple 1:1:1 triplet of 1:1:1 triplets, the value of $a_{CD_3}^D$ being less than the linewidth. The e.s.r. data obtained are included in Table 11. The temperature coefficients of the hyperfine coupling constants are in accord with our previous analysis,¹⁴ that is, out-of-plane bending about the sulphur-sulphur axis occurs and that $a^{N(2)}$ is positive while the other coupling constants are negative. Reddoch *et al.*³⁴ have considered the case of the out-of-plane motion of a single proton attached to a planar carbon ring system. They showed that positive spin density on a carbon atom leads to a negative value of a^H and, consequently, the temperature dependence of a^H is also negative. These predictions have been found to be of general applicability.

The presence of fine structure additional to that from the nitrogen in position 2 made it very difficult to observe splittings from natural abundance sulphur-33; previously¹⁴ we have found that observation of couplings from the latter isotope is simple.

Cyclic Voltammetry.—All the salts showed perfectly reversible redox behaviour. Peak potentials (E^p) for the

reductive and oxidative phases of the cycle are listed in Table 12. The potentials show the expected 60 mV for a one-electron process at room temperature. E° values have been taken as the mean of E_{ox}^p and E_{red}^p .

Molecular-orbital Calculations.—Molecular-orbital calculations were carried out using a Gaussian 76 computer program³⁵ having a STO-3G basis set, and an INDO program based on that devised by Pople³⁶ and modified³⁷ to allow its use with second-row elements.

Minimum-energy geometries were obtained for 1,3,2-dithiazolium and its radical using INDO and Gaussian 76 and for 5-methyl-1,3,2,4-dithiazolium and its radical using the INDO method only, as the Gaussian calculations failed to converge. The bond distances and angles obtained are listed in Table 13 where they are compared with those found by X-ray crystallography. The agreement between calculated and experimental values is reasonable for the cations; hence it may be assumed that the molecular parameters calculated for the radicals are reliable. The INDO and Gaussian minimum-energy structures were used to calculate the e.s.r. coupling constants by the INDO method (see Table 14); in the case of 4-methyl-1,3,2-dithiazol-2-yl, the ring dimensions for 1,3,2-dithiazol-2-yl were taken in conjunction with standard bond lengths and angles for the methyl substituent. The difficulty of observing satellite lines from the low-abundance magnetic nuclei led to the paucity of experimental data in Table 14. However, the agreement between experimental and calculated values is good apart from the sulphur-33 hyperfine coupling constants. It is our intention to supplement the experimental data by isotopic labelling of the radicals.

We have calculated the stabilities of the cations relative to the radicals derived from them by comparing the energies of the minimum-energy molecular-orbital structures: the values obtained are presented in Table 15. The energies of stabilization ($E_{radical} - E_{cation}$) are negative which suggests that the radicals are more stable than their cations without their counter ions. The 5-methyl-1,3,2,4-dithiazol-2-yl radical is the most stable with respect to its cation, a result supported qualitatively by the observed longer life of this radical. This finding contradicts the cyclic voltammetry results (Table 12), but it must be re-

Table 12. Electrochemical data^a from cyclic voltammetry at 20 °C in acetonitrile containing 0.1 mol dm⁻³ NBu₄BF₄

Compound	E_{ox}^p/V	E_{red}^p/V	E°/V
HCSNSCH ⁺ AsF ₆ ⁻	+0.05	-0.01	+0.02
CH ₃ CSNSCH ⁺ AsF ₆ ⁻	-0.60	-0.66	-0.63
CH ₃ CSNSN ⁺ AsF ₆ ⁻	-0.23	-0.29	-0.26

^a Ag-Ag⁺ (0.01 mol dm⁻³ in acetonitrile) reference electrode.

Table 13. Minimum-energy structures and X-ray data

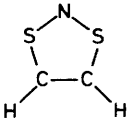
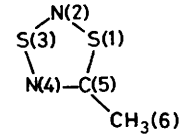
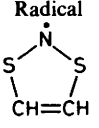
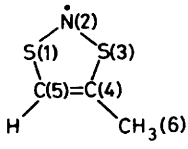
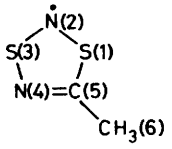
Bond lengths (Å) and angles (°)	Minimum-energy values for the radical		Minimum-energy values for the cation		X-Ray data for the cation	
	INDO	Gaussian	INDO	Gaussian		
	S-N	1.72	1.71	1.68	1.60	
	C-S	1.85	1.80	1.81	1.68	
	C-C	1.36	1.30	1.34	1.40	
	S-N-S	110.8	109.2	115.0	112.2	
	C-S-N	101.1	100.9	98.0	102.0	
	C-C-S	113.5	114.5	114.5	111.8	
	S(1)-N(2)	1.73	—	1.71	—	1.63
	N(2)-S(3)	1.73	—	1.72	—	1.59
	S(3)-N(4)	1.79	—	1.83	—	1.57
	N(4)-C(5)	1.30	—	1.26	—	1.32
	C(5)-S(1)	1.79	—	1.81	—	1.77
	C(5)-C(6)	1.45	—	1.51	—	1.46
	S(1)-N(2)-S(3)	109.5	—	113.0	—	110.4
	N(2)-S(3)-N(4)	101.3	—	100.0	—	105.0
	S(3)-N(4)-C(5)	111.5	—	111.0	—	116.0
	N(4)-C(5)-S(1)	120.5	—	125.0	—	111.0
	C(5)-S(1)-N(2)	97.2	—	94.0	—	98.4
	N(4)-C(5)-C(6)	119.8	—	122.0	—	127.0

Table 14. Calculated (INDO) and experimental e.s.r. coupling constants (mT) of the radicals

Radical	Coupling constant	Calculated from minimum-energy structure		Experimental
		INDO	Gaussian	
	a^N	+1.111	+1.120	+1.071 ^a
	a^S	+0.070	+0.166	—
	a^C	-0.037	-0.049	—
	a^H	-0.063	-0.068	-0.134 ^a
	$a^{N(2)}$	+1.107	+1.216	+1.065 ^b
	$a^{S(1)}$	+0.071	+0.166	—
	$a^{S(3)}$	+0.071	+0.166	—
	$a^{C(4)}$	-0.042	-0.053	—
	$a^{C(5)}$	-0.031	-0.044	—
	a^H	-0.064	-0.068	-0.150 ^b
	$a_{CH_3}^H$	-0.008	-0.009	-0.0286 ^c
	$a^{N(2)}$	+1.096	—	+1.110 ^d
	$a^{S(1)}$	+0.071	—	{ 0.518 and 0.372 ^e
	$a^{S(3)}$	+0.119	—	
	$a^{N(4)}$	+0.017	—	
	$a^{C(5)}$	-0.111	—	0.0647 ^f
	$a_{CH_3}^H$	-0.079	—	0.0613 ^f

^a Radical in toluene at +20.2 °C. ^b Radical in toluene at +20.3 °C. ^c Radical in toluene at -94.3 °C. ^d Radical in thf at -34.3 °C. ^e Satellite lines from spectrum of radical in toluene at +3.3 °C. ^f Radical in thf at -85.4 °C.

Table 15. INDO calculations of the binding energies (a.u.) of the radicals and cations

Compound	E_{radical}	E_{cation}	$E_{\text{radical}} - E_{\text{cation}}$
HCSNSCH	-1.0209	-0.7079	-0.3130
CH ₃ CNSNSCH	-1.7111	-1.3695	-0.3416
CH ₃ CNSNSN	-2.2549	-1.9415	-0.3134

membered that the presence of solvent, and the larger AsF₆⁻ counter ion, gives an extra stability to the cations which is ignored by the INDO calculations.

The related RCN₂SSN radicals (R = CH₃, Ph, or CCl₃)⁸ readily dimerize and exist as discrete dimers in the solid state, usually linked together *via* the disulphide bonds. Preliminary attempts to prepare CH₃CNSNSN and RCSNSCH (R = H or CH₃) neutral species as solids at room temperature have been unsuccessful.

Acknowledgements

We (G. K. M., J. P., M. N. S., M. J. S., and P. S. W.) thank the N.S.E.R.C. (Canada) for financial support, Mr. R. Coult for elemental analysis, and Dr. A. J. Banister for useful discussions. We also thank Dr. L. Calhoun for the n.m.r. spectra. J. P. thanks N.A.T.O. for a travel grant.

References

- 1 A. J. Banister, R. G. Hey, G. K. MacLean, and J. Passmore, *Inorg. Chem.*, 1982, **21**, 1679.
- 2 C. H. Chen and B. A. Donatelli, *J. Heterocycl. Chem.*, 1979, **16**, 183.
- 3 S. T. A. K. Daley, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1984, 57.
- 4 P. Hope and L. A. Wiles, *Chem. Commun.*, 1967, 1642; R. Mayer, S. Bleisch, and G. Domschke, *Z. Chem.*, 1978, **18**, 323.
- 5 I. Shinbaya, *Nippon Kagaku Kaishi*, 1979, 389 (*Chem. Abstr.*, 1979, **90**, 186869).
- 6 Wolmershäuser, C. Krüger, and Y. H. Tsay, *Chem. Ber.*, 1982, **115**, 1126.

- 7 F. A. Kennett, G. K. MacLean, J. Passmore, and W. M. S. Rao, *J. Chem. Soc., Dalton Trans.*, 1982, 851.
- 8 A. J. Banister, N. R. M. Smith, and R. G. Hey, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1181.
- 9 G. G. Alange, A. J. Banister, B. Bell, and P. W. Millen, *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 143; *J. Chem. Soc., Perkin Trans. 1*, 1979, 1192.
- 10 H. U. Höfs, R. Mews, W. Llegg, M. Noltemeyer, M. Schmidt, and A. M. Sheldrick, *Chem. Ber.*, 1983, **116**, 416.
- 11 O. Andreasen, A. C. Hazell, and R. G. Hazell, *Acta Crystallogr., Sect. B*, 1977, **33**, 1109.
- 12 H. W. Roesky and T. Müller, *Chem. Ber.*, 1978, **111**, 2960.
- 13 S. A. Fairhurst, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans. 1*, 1983, 439.
- 14 S. A. Fairhurst, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans. 1*, 1983, 925.
- 15 G. K. MacLean, J. Passmore, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1983, 807.
- 16 A. C. Larson and E. J. Gabe, 'Minimum Computer System for Complete Structure Determination,' in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazelkamp, H. van Koningsveld, and G. C. Bassi, Delft University Press, The Netherlands, 1978, pp. 81-89.
- 17 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.
- 18 'International Tables of X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
- 19 G. M. Sheldrick, SHELX, A Program for Crystal Structure Determination, University of Cambridge, 1976.
- 20 S. A. Fairhurst, W. R. McIlwaine, and L. H. Sutcliffe, *J. Magn. Reson.*, 1979, **35**, 121.
- 21 S. A. Fairhurst and L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans. 1*, 1980, 1496.
- 22 G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.
- 23 G. Peyronel, A. Pignedoli, and W. Malavasi, *Spectrochim. Acta, Part A*, 1982, **38**, 971.
- 24 H. W. Roesky, W. Wehner, E.-J. Zehnder, H.-J. Dieseroth, and A. Simon, *Chem. Ber.*, 1978, **111**, 1670.
- 25 A. Gieren, B. Dederer, R. Martin, F. Schanda, H. W. Roesky, and M. Eiser, *Chem. Ber.*, 1980, **113**, 3904.
- 26 H. W. Roesky, M. Thomas, M. Noltemeyer, and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 858.
- 27 A. J. Banister, *Phosphorus Sulphur*, 1978, **5**, 147.

- 28 A. J. Banister, *Nature (London), Phys. Sci.*, 1972, **237**, 92; W. L. Jolly, 'Sulphur Research Trends,' *Adv. Chem. Ser.*, 1972, **110**, 92.
- 29 S. C. Nyberg, *J. Cryst. Mol. Struct.*, 1973, **3**, 331.
- 30 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960, p. 239.
- 31 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
- 32 R. E. Rosenfield, Jr., R. Parthasarathy, and J. D. Dunitz, *J. Am. Chem. Soc.*, 1977, **99**, 4860.
- 33 S. R. Harrison, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans. 1*, 1984, 669.
- 34 A. H. Reddoch, C. L. Dodson, and D. M. Paskovich, *J. Chem. Phys.*, 1978, **52**, 2318.
- 35 Program No. 368, Quantum Chemistry Exchange, Bloomington, Indiana, 1976.
- 36 J. A. Pople, Program No. 141, Quantum Chemistry Exchange, Bloomington, Indiana, 1967.
- 37 M. D. Beer and R. Grinter, *J. Magn. Reson.*, 1977, **26**, 421.
- 38 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' John Wiley and Sons, New York, 1958.
- 39 S. D. Ross, 'Inorganic Infrared and Raman Spectra,' McGraw-Hill, Maidenhead, 1972.
- 40 A. Gieren and B. Dederer, *Acta Crystallogr., Sect. B*, 1978, **34**, 2046.

Received 17th May, 1984; Paper 4/812