Preparation and Characterisation of the Mixed 1,3,2,4-/1,2,3,5-Dithiadiazolylium Salts and Related Free Radicals; $[m\text{- and }[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^x$ (x = 2+, •+ or 2•)†

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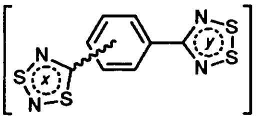
The salts $[m\text{- and }[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]_2$ were prepared (in yields exceeding 90%) by the reaction of $[NCC_6H_4\overline{CNSSN}][AsF_6]$ with $[SNS][AsF_6]$ in liquid SO_2 and were recrystallised as MeCN solvates. Partial and complete reduction of these dications (as the dichloride salts) led to the isolation and solid-state characterisation of the paramagnetic radical cations $[m\text{- and }[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl$ and the diradicals $[m\text{- and }[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-})\overline{CNSSN}^{2\bullet}$. The crystal structure of $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]_2\cdot MeCN$ shows essentially planar $\overline{SNSNC}$ and $\overline{CNSSN}$ rings, rotated by 25.1 and 16.7° respectively from the phenylene ring plane.

Recent advances[1-3] in the chemistry[4] of dithia- and diselenadiazolylium salts and their related free radicals have centred on the development of these materials as organic metals;[1,2] the formation of a conduction band by overlap of singly occupied molecular orbitals (SOMOs) of neutral radicals (such as dithiadiazolyl radicals) was initially proposed by Haddon.[5] We have previously attempted to achieve similar stacking conformations in dithiadiazolylium charge-transfer salts,[6] *e.g.* $[Ph\overline{CNSSN}]_2[M(mnt)_2]$ [M = Pt, Cu or Ni; mnt = maleonitriledithiolate (*cis*-1,2-dicyanoethylene-1,2-dithiolate). High-symmetry dithiadiazolyl and dithiadiselenazolyl radicals, prepared by reduction of multi-(dithiadiazolylium) and -(diselenadiazolylium) cations,[1-3] are also of interest because of possible co-operative magnetic behaviour, *viz* antiferro-, ferro- or ferri-magnetic coupling. A summary of recent work on compounds containing more than one CN_2S_2 ring is given in Table 1.

In a preliminary communication[1d] we recently reported the synthesis of the mixed 1,3,2,4/1,2,3,5 salt $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]_2$, the corresponding diradical $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{2\bullet}$ and proposed the isolation of the intermediate radical cation, $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{\bullet +}$. We now report full details of this work including the crystal structure of $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]_2\cdot MeCN$ and the solid-state and solution properties of the radical cations **2** and diradicals **3**.

Results and Discussion

Oakley and co-workers[2] have previously shown that the reaction of persilylated amidines $RC(=NSiMe_3)N(SiMe_3)_2$ with either SCl_2 or $SeCl_2$ (formed *in situ* from $SeCl_4$–Se or $SeCl_4$–$SbPh_3$) provides a convenient, high-yield route to aryl 1,2,3,5-dithiadiazolylium and -diselenadiazolylium salts. In some cases (R = p-$O_2NC_6H_4$ or p-NCC_6H_4) the preparation of the above amidine was not possible, despite the apparently quantitative (^{1}H NMR spectroscopy) formation of the precursor *N*-lithio compound, *e.g.* $Li[NCC_6H_4C(NSiMe_3)_2]$.[10] However, we have found that reaction of these *N*-lithio intermediates with a slight excess of SCl_2 provided the dithiadiazolylium chloride in high yield (typically > 70%).[11] In the case of the mono(dithiadiazolylium) derivatives the dithiadiazolylium chlorides obtained were readily recovered from LiCl by extraction with liquid SO_2 and then washed with CH_2Cl_2 (to remove any unreacted SCl_2).[11] In the case of $[m\text{- and }[p\text{-}NCC_6H_4\overline{CNSSN}]Cl$, recovered yields were in excess of 70%.



x y
1 + + **a** *para*
2 + • **b** *meta*
3 • •

Metathesis of these chloride salts with $Ag[AsF_6]$ (in liquid SO_2) provided the hexafluoroarsenate(v) salts, $[m\text{- and }[p\text{-}NCC_6H_4\overline{CNSSN}][AsF_6]$ whilst reduction with $SbPh_3$ led to the corresponding dithiadiazolyl radicals (m- and (p-NCC_6H_4-$\overline{SNSSN}$)$_2$ in high yield. (A full structural characterisation of these radicals, prepared by Oakley and co-workers[2e] from cyanobenzamidine precursors, has been published recently.) The subsequent reactions of these materials, {*i.e.* $[NCC_6H_4\overline{CNSSN}]Cl$, $[NCC_6H_4\overline{CNSSN}][AsF_6]$ and $(NC\text{-}C_6H_4\overline{CNSSN})_2$} with $[SNS][AsF_6]$ were then examined, in an attempt to prepare the corresponding mixed 1,3,2,4-/1,2,3,5-dithiadiazolylium dications and (in the third case) radical cations.

Reaction of $[SNS][AsF_6]$ with $[p\text{-}NCC_6H_4\overline{CNSSN}]Cl$ did not yield the anticipated mixed chloride–hexafluoroarsenate salt, $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl[AsF_6]$, but rather $[p\text{-}NC\text{-}C_6H_4\overline{CNSSN}][AsF_6]$ (IR and elemental analysis), together with a red-green insoluble product (shown to be $[S_3N_2]Cl$ by IR spectroscopy) and a red, soluble, volatile component. Such reaction products can be considered to arise through

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: emu = SI × $10^6/4\pi$.

Table 1 A summary of previously reported multi(dithiadiazolylium) cations and multi(dithiadiazolyl) radicals

(*a*) Multi(1,3,2,4-dithiadiazol-yl/-ylium salts

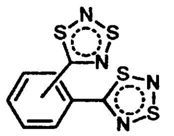
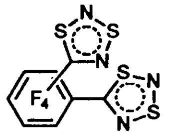
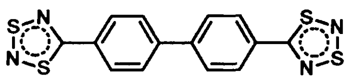
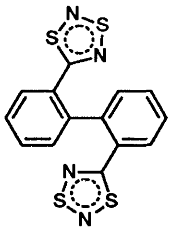
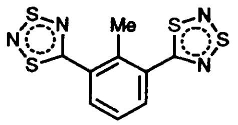
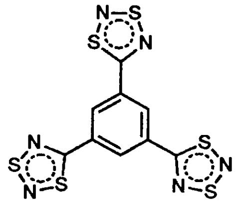
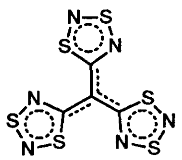
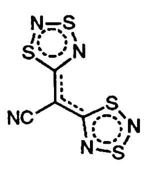
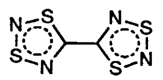
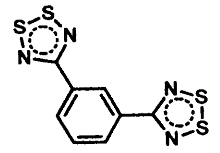
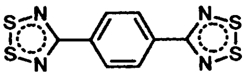
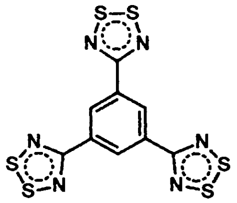
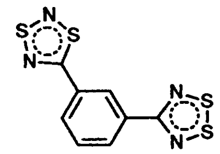
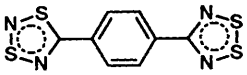
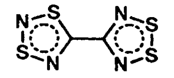
		Cation (as the AsF_6^- salt)			Radical		
		Yield (%)	Analysis	Ref.	Yield (%)	Analysis	Ref.
	*para-*	92	*a,b*	1(*a*)	90	*a,c,d*	1(*a*)
	meta-	85	*a,b*	1(*a*)	59	*a,c*	1(*c*)
	ortho-	75	*a,b*	1(*a*)	—	*c*	
	*para-*	96	*a,e*	7	—	*c*	7,*f*
	meta-	95	*a,e*	7	—	*c*	7,*f*
	ortho-	94	*a,e*	7	—	*c*	7,*f*
		79	*a,b*	1(*c*)	76	*a,c*	1(*c*)
		84	*a,b*	7	—	*c,f*	8
		92	*a,b*	7	62	*a,c*	7
		96	*a,b*	1(*c*)	72	*a,c*	1(*c*)
		84	*a,d,g*	1(*b*)	—	*c*	1(*c*)
		59	*a,g*	1(*b*)	—	*c*	8
		97	*a,d,g*	3	84	*a*	3

Table 1 (*Continued*)

(*b*) Multi(1,2,3,5-dithiadiazol-yl/-ylium) salts

	Cation (as the Cl$^-$ salt)			Radical		
	Yield (%)	Analysis	Ref.	Yield (%)	Anslysis	Ref.
	?	?	2(*b*)	78	*a,c,d*	2(*b*), 1(*c*)
	65	*a,d,h*	2(*a*)	32	*a,c,d*	2(*a*), 1(*c*)
	*f*	*f*	9	40	*a,d*	1(*c*), 9

(*c*) Mixed (1,3,2,4-/1,2,3,5-dithiadiazol-yl/-ylium) salts

	Cation (as the AsF$_6^-$ salt)			Radical		
	Yield	Analysis	Ref.	Yield (%)	Analysis	Ref.
	94	*a*	This work	43	*a,c*	This work
	97	*a,b,d*	This work	78	*a,c*	This work
	39	*a,d,e*	3	—	—	—

[a] Satisfactory elemental analysis. [b] ^{1}H NMR. [c] ESR. [d] Crystal structure determination. [e] ^{19}F NMR. [f] Not isolated. [g] ^{13}C and/or ^{14} NMR. [h] As SbF$_6^-$ salt.

an initial metathesis step, forming [SNS]Cl and [*p*-NCC$_6$H$_4$CNSSN][AsF$_6$] and then decomposition of [SNS]Cl to give [S$_3$N$_2$]Cl and S$_2$Cl$_2$ (see Scheme 1). In a somewhat analogous fashion, reaction of [SNS][AsF$_6$] with (*p*-NCC$_6$H$_4$CNSSN)$_2$ produced a yellow solid [*p*-NCC$_6$H$_4$CNSSN][AsF$_6$] (IR and elemental analysis), unreacted (*p*-NCC$_6$H$_4$CNSSN)$_2$ and a red oil (presumably S$_4$N$_2$) which on standing yielded small red crystals (S$_4$N$_4$ by IR spectroscopy) and sulfur (see Scheme 1). In contrast, reaction of [*m*- and [*p*-NCC$_6$H$_4$CNSSN][AsF$_6$] with [SNS][AsF$_6$] in liquid SO$_2$ yielded the desired mixed 1,3,2,4-/1,2,3,5-dithiadiazolylium salts in almost quantitative (>90% recovered) yields. Recrystallisation of [*m*- and [*p*-SNSNC–C$_6$H$_4$–CNSSN][AsF$_6$] from MeCN–C$_6$H$_4$Cl$_2$-*o* by slow removal of MeCN under a temperature gradient yielded long thin crystals of the hexafluoroarsenate(v) salts as MeCN solvates.

Structure.—The crystal structure of [*p*-SNSNC–C$_6$H$_4$–CNSSN][AsF$_6$]$_2$·MeCN shows 1,2,3,5- and 1,3,2,4-dithiadiazolylium rings held together through a phenylene unit (Fig. 1). Bond distances and angles in both dithiadiazolylium rings

$$[p\text{-NCC}_6\text{H}_4\text{CNSSN}]\text{Cl} + [\text{SNS}][\text{AsF}_6] \xrightarrow{(i),(ii)} [\text{SNS}]\text{Cl} \longrightarrow \tfrac{1}{2}[\text{S}_3\text{N}_2]\text{Cl} + \tfrac{1}{2}\text{S}_2\text{Cl}_2$$

$$(p\text{-NCC}_6\text{H}_4\text{CNSSN})_2 + 2[\text{SNS}][\text{AsF}_6] \xrightarrow{(i),(ii)} 2[\text{SNS}]^\bullet \longrightarrow \text{S}_4\text{N}_2 \longrightarrow \tfrac{1}{2}\text{S}_4\text{N}_4 + \tfrac{1}{4}\text{S}_8$$

$$[p\text{-NCC}_6\text{H}_4\text{CNSSN}][\text{AsF}_6] + [\text{SNS}][\text{AsF}_6] \xrightarrow{(i)} [\text{SNSNC–C}_6\text{H}_4\text{–CNSSN}][\text{AsF}_6]_2$$

Scheme 1 Reactions of [SNS][AsF$_6$] with *p*-cyanophenyldithiadiazol-yl/-ylium salts. (*i*) Liquid SO$_2$; (*ii*) $-$[NCC$_6$H$_4$CNSSN][AsF$_6$]

Table 2 Comparison of the dithiadiazolylium bond distances and angles in [p-SNSNC–C$_6$H$_4$–CNSSN][AsF$_6$]$_2$·MeCN with those in related 1,2,3,5- and 1,3,2,4-dithiadiazolylium cations

	1,3,2,4-Dithiadiazolylium			1,2,3,5-Dithiadiazolylium		
	[PhCNSNS]-[AsF$_6$]	[p-SNSNC–C$_6$H$_4$–CNSSN]-[AsF$_6$]$_2$·MeCN		[p-SNSNC–C$_6$H$_4$–CNSSN]-[AsF$_6$]$_2$·MeCN	[C$_6$H$_4$(CNSSN)$_2$-p]-[SbF$_6$]$_2$·2PhCN	[PhCNSSN]-[AsF$_6$]
Bond distance (Å)						
C–N	1.336(9)	1.313(11)	C–N	1.339(10)	1.334(12)	1.337(6)
N–S	1.576(7)	1.583(7)		1.351(11)	1.345(13)	1.354(6)
S–N	1.561(8)	1.568(9)	N–S	1.571(8)	1.576(9)	1.563(4)
N–S	1.596(8)	1.606(8)		1.582(7)	1.577(9)	1.573(5)
S–C	1.732(8)	1.732(9)	S–S	2.019(4)	2.009(4)	2.023(2)
Bond angle (°)						
S–C–N	111.9(6)	113.6(6)	N–C–N	118.7(8)	119.0(9)	117.4(4)
C–N–S	114.3(5)	113.4(6)	C–N–S	114.9(6)	114.6(7)	116.0(3)
N–S–N	103.3(4)	103.6(4)		115.7(6)	115.3(8)	116.4(4)
S–N–S	113.1(4)	112.6(4)	N–S–S	95.4(3)	95.3(4)	94.8(2)
N–S–C	94.7(4)	96.7(4)		95.4(3)	95.6(4)	95.3(2)
Twist angle (°)	23	25.1		16.7	15.8	0
Ref.	14	This work		This work	13	12

are similar to those observed in related structures (see Table 2). The 1,2,3,5-dithiadiazolylium ring possesses bond lengths identical (within 0.01 Å) to those of the related [PhCNSSN]-[AsF$_6$][12] and [C$_6$H$_4$(CNSSN)$_2$-p][SbF$_6$]$_2$·2PhCN[13] cations. Although the CNSSN ring is completely planar within experimental error [root-mean-square (r.m.s.) deviation, Δ = 0.001 Å], it is twisted some 16.7° out of plane with respect to the phenylene ring, similar to the twist angle observed in [C$_6$H$_4$-(CNSSN)$_2$-p][SbF$_6$]$_2$·2PhCN (θ = 15.8°) but different from the essentially planar cation in [PhCNSSN][AsF$_6$]. Such rotation out of the molecular plane perhaps arises through a combination of secondary interactions and molecular packing forces. For example, [p-ClC$_6$H$_4$CNSSN][AsF$_6$][14] (analogous to [PhCNSSN][AsF$_6$]) does show a twist angle [θ = 21.9(2)°] between the phenylene and dithiadiazolylium rings. Indeed MO calculations[8] have shown that the energy barrier to rotation about the C–C bond in such systems is low (below kT at room temperature) when the twist angle remains less than about 30°.

In a similar manner, the 1,3,2,4-dithiadiazolylium ring shows comparable bond distances (within 0.02 Å) to those found in [PhCNSNS][AsF$_6$][15] with the most marked difference being a slight shortening of the C–N distance at 1.3(11) Å (see Table 2). The CNSNS ring is also essentially planar (r.m.s. deviation, Δ = 0.011 Å). In comparison to [C$_6$H$_4$(CNSSN)$_2$-p][SbF$_6$]$_2$·2PhCN which shows an inversion centre (*i.e.* the two dithiadiazolylium rings are twisted in opposite senses to the phenylene plane), the mixed dication shows both rings twisted in the same sense, the 1,3,2,4-dithiadiazolylium ring being twisted by 25.1° with respect to the phenylene plane. This twist angle is similar to that observed[15] in [PhCNSNS][AsF$_6$] [23.1(9)°].

The solvate molecule in [p-SNSNC–C$_6$H$_4$–CNSSN]-[AsF$_6$]$_2$·MeCN appears to be associated with the 1,2,3,5-dithiadiazolylium ring; the acetonitrile N atom is in the CNSSN ring plane and shows close contacts to S(3) and S(4) at 2.73 and 2.81 Å respectively (Fig. 2). However the energy change associated with charge transfer from MeCN is probably low, because the perturbation of the S–S bond length (which can arise through in- or out-of-plane interactions[4b]) is negligible. The S–S distance, 2.019(4) Å, in [p-SNSNC–C$_6$H$_4$–CNSSN] [AsF$_6$]$_2$·MeCN is the same as that in [PhCNSSN][AsF$_6$] [2.023(1) Å].[1] It is longer than that in [PhCNSSN]Cl[17] [1.990(5) Å] where there are appreciable in-plane interactions. The presence of two solvate molecules in [C$_6$H$_4$(CNSSN)$_2$-p]-[SbF$_6$]$_2$·2PhCN indicates stronger solvent interactions with the 1,2,3,5- than the 1,3,2,4-dithiadiazolylium ring, *i.e.* solvent molecules, like anions, interact more strongly with the 1,2,3,5-dithiadiazolylium ring in which there are adjacent sulfur atoms.

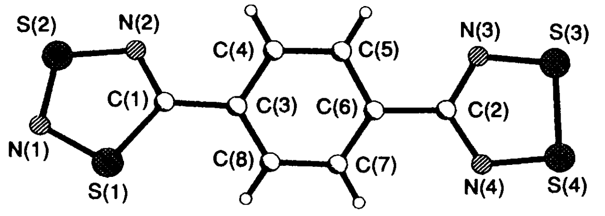


Fig. 1 Structure of the dication in [p-SNSNC–C$_6$H$_4$–CNSSN]-[AsF$_6$]$_2$·MeCN showing atom labelling

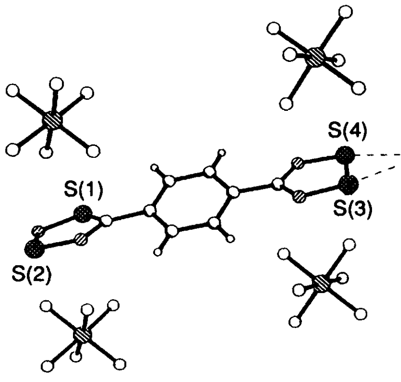


Fig. 2 Solvent interactions with the 1,2,3,5-dithiadiazolylium cation in [SNSNC–C$_6$H$_4$–CNSSN][AsF$_6$]$_2$·MeCN. The closest anions sandwiching the heterocyclic rings are also shown

Cyclic Voltammetry.—Cyclic voltammetry (CV) studies on bis(1,3,2,4-dithiadiazolylium)andbis(1,2,3,5-dithiadiazolylium) cations[1a,2c] have shown essentially non-interacting dithiadiazolylium rings in which two-electron reduction is either concerted or takes place over a small potential range (< 0.01 V). In comparison, cyclic voltammograms of [p-SNSNC–C$_6$H$_4$–

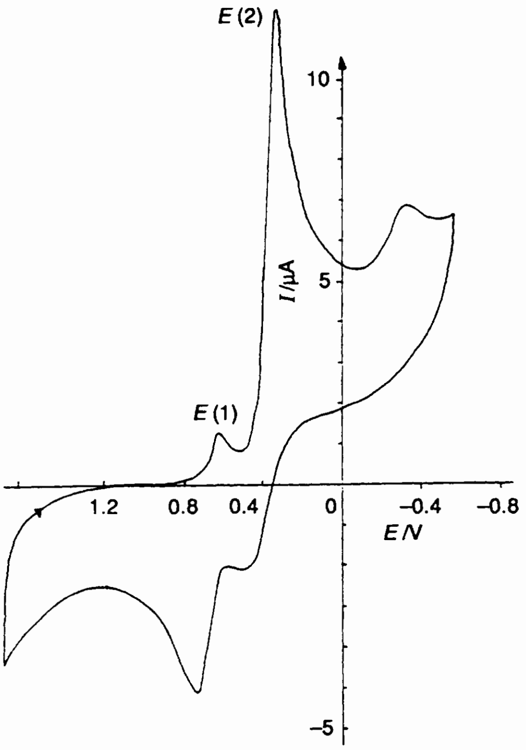


Fig. 3 Cyclic voltammogram of $[m\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]_2$ in MeCN at −10 °C with $[NBu_4][BF_4]$ as supporting electrolyte. $E_{red}(1) = +0.647$, $E_{red}(2) = +0.387$ V, *vs.* standard calomel electrode.

$\overline{CNSSN}][AsF_6]_2$ [1d] and $[m\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]_2$ in MeCN at *ca.* −10 °C, using $[NBu_4][BF_4]$ as supporting electrolyte, show sequential reduction to the corresponding radical cation and then the diradical. The difference in reduction potentials (0.28 ± 0.03 V) for the formation of the radical cation and diradical suggested that isolation of the intermediate radical cations would be possible (as described herein). Comparison of the CV data for the mixed 1,3,2,4-/1,2,3,5-dithiadiazolylium cations and other simple 1,3,2,4- and 1,2,3,5-dithiadiazolylium cations indicates that the first reduction, $E(1)$, can be attributed to the $\overline{CNSSN}$ ring and the second, $E(2)$, to the $\overline{CNSNS}$ ring (Fig. 3).

Electron Spin Resonance.—Partial reduction (using an excess of salt and a deficit of $SbPh_3$, or $[NBu_4]I$) of the dications $[m$- or $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl_2$ gave the expected 1:2:3:2:1 pentet associated with formation of the 1,2,3,5-dithiadiazolyl radical (Fig. 4).[4b] Such a spectrum is indicative* of the formation of $[\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{\bullet+}$. There was no observable indication of spin leakage from the 1,2,3,5 to the isomeric 1,3,2,4 ring on either warming or cooling. Indeed the simple pentet spectrum had comparable ESR parameters to those of other aryl mono(1,2,3,5-dithiadiazolyl) radicals (g = 2.01, a_N = 0.5 mT).[18]

Complete reduction (using an excess of $SbPh_3$) of these radical cations showed a 1:2:3:2:1 pentet overlapping the 1:1:1 triplet, indicative of the diradical $[\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{2\bullet}$. On warming there was no evidence for spin–spin exchange bands observed in other multi(dithiadiazolyl) radicals[2a,b,7] but rearrangement was observed on stronger heating to give the previously reported $[\overline{NSSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{2\bullet}$ systems[2a,b] (g = 2.011, a_N = 0.51 mT). Such a process has previously been described in terms of a thermal[19] or photochemical[20] bimolecular rearrangement.

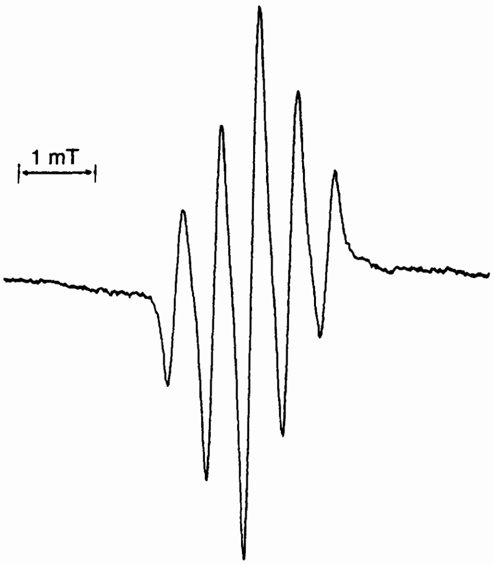


Fig. 4 Electron spin resonance spectrum of the radical cation $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{\bullet+}$ in C_6H_5Me at room temperature (g = 2.01, a_N = 0.5 mT)

Preparative-scale Reductions.—Metathesis of $[m$- and $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]$ with 2 equivalents of $[NBu_4]Cl$ provided the dichloride salts $[\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl_2$, which were then reduced with 0.5 or 1 equivalent of $SbPh_3$ to yield the radical cations $[m$- and $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl$ and the diradicals $[m$- and $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{2\bullet}$ respectively [equation (1)]. The radical cations (as

$$2[\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl_2 \xrightarrow[-SbPh_3Cl_2]{+SbPh_3} 2[\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl \xrightarrow[-SbPh_3Cl_2]{+SbPh_3} 2[\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{2\bullet} \quad (1)$$

the chloride salts) were isolated as dark purple and green solids (m and p respectively) whereas the diradicals were deeper in colour (purple-black and black) and significantly more moisture sensitive.

In comparison, attempts to prepare the radical cation $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]$ by metathesis of the dication $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]_2$ with 1 equivalent of $[NBu_4]Cl$, followed by reduction with $SbPh_3$, were unsuccessful; reaction of 1 equivalent of $[NBu_4]Cl$ with $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}][AsF_6]_2$ yielded a salt analysing as $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl_{1.5}[AsF_6]_{0.5}$. Similar salts, such as $[Ph\overline{CNSSN}]_3Cl[AsF_6]_2$, have been observed previously.[12] Conversely, metathesis of $[m\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl_2$ with 1 equivalent of $Ag[AsF_6]$ followed by reduction gave red-brown products with variable elemental analysis.

Attempts to crystallise $[p\text{-}\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{2\bullet}$ by high-vacuum sublimation [10^{-7} Torr (*ca.* 1.33 × 10^{-5} Pa), 110 °C], electrocrystallisation (under constant current or fixed potential on a variety of substrates) and slow diffusion-controlled reactions (using $[\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]Cl_2$,

---

* The ESR spectra of the radical cations $[\overline{SNSNC}\text{-}C_6H_4\text{-}\overline{CNSSN}]^{\bullet+}$, which were analytically pure (showing no ν_{CN} bands or other evidence of hydrolysis), were identical to those spectra observed for materials prepared *in situ* and thus cannot readily be attributed to impurities and/or decomposition products.

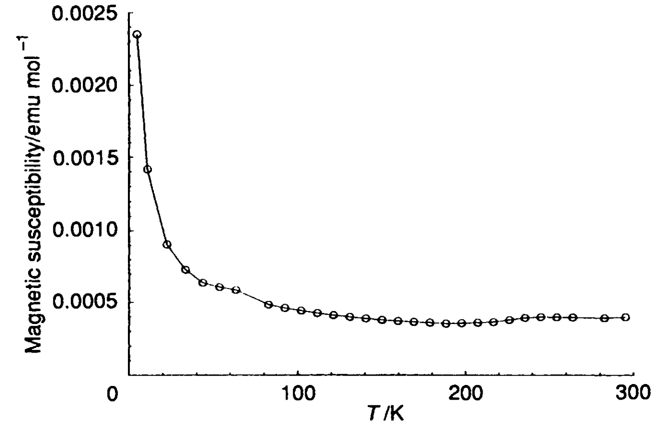


Fig. 5 Variation of the magnetic susceptibility as a function of temperature for the diradical [p-SNSNC–C$_6$H$_4$–CNSSN]$^{2\cdot}$

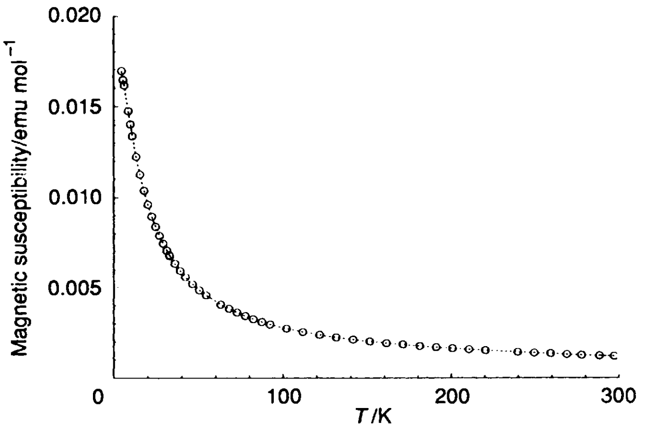


Fig. 6 Variation of the magnetic susceptibility as a function of temperature for the radical cation [p-SNSNC–C$_6$H$_4$–CNSSN]Cl

SbPh$_3$ and various solvents) were unsuccessful, although the diffusion methods provided microcrystalline samples. As yet similar attempts to grow crystals of the radical cation salt [p-SNSNC– C$_6$H$_4$–CNSSN]Cl have also been unsuccessful.

Magnetisation Measurements.—Fig. 5 shows the variation of magnetic susceptibility of the neutral mixed diradical [p-SNSNC–C$_6$H$_4$–CNSSN]$^{2\cdot}$ with temperature. A fit to Curie–Weiss law behaviour can be made for the paramagnetic tail in the susceptibility plot, provided a constant corrective factor of -1.0×10^{-4} emu mol^{-1} is made. The latter contribution is believed to be due to a small concentration of ferromagnetic impurity and is likely to be responsible for the small magnetic structure (Fig. 5) observed in the susceptibility around 60 K. Magnetic susceptibility with characteristic Curie-tail behaviour has previously been observed for related bis(dithiadiazolyl) radicals.[2a,b,d,7] Spin-paired bonding interactions between dithiadiazolyl radicals in the solid state lead to a diamagnetic dimer in the bis(1,2,3,5-dithiadiazolyl), p-NSSNC–C$_6$H$_4$–CNSSN,[2a] and a diamagnetic polymer in the bis(1,3,2,4-dithiadiazolyl) p-SNSNC–C$_6$H$_4$–CNSNS [1a]. The residual paramagnetic response of the latter two materials is attributable to the unpaired spins at lattice defects or polymer-chain ends respectively and varies between 1 and 16% unpaired spins per molecule depending upon the degree of crystallinity.[2] In comparison the spin concentration per molecule in p-SNSNC–C$_6$H$_4$–CNSSN can be estimated at 3% assuming a Curie–Weiss fit.

In contrast the radical cation (as the chloride salt), [p-SNSNC–C$_6$H$_4$–CNSSN]Cl is strongly paramagnetic with antiferromagnetic interactions (Fig. 6); a plot of χ^{-1} *versus* temperature shows that the material follows a Curie–Weiss type behaviour above 160 K with $\theta = -65$ K. The effective magnetic moment at higher temperatures can thus be estimated at 1.87, somewhat in excess of the 1.73 expected of a spin $\frac{1}{2}$ system with a g factor close to 2. Such a strong paramagnetic response from dithiadiazolyl radicals in the condensed phase is rare and has previously only been observed for liquid dithiadiazolyl radicals[20,21] and the salts [RCNSSN]$_3$Cl (R = Cl or CF$_3$).[22] However, similar data have recently been observed by Passmore and co-workers[23] for their related radical cations [CF$_3$CNSSS][AsF$_6$] and [CF$_3$CSSSCCF$_3$]-[AsF$_6$]. Our Gouy balance data, on the *meta* systems [m-NSNSC–C$_6$H$_4$–CNSSN]Cl and [m-NSNSC–C$_6$H$_4$–CNSSN]$_2$ indicate paramagnetism and diamagnetism (respectively) at room temperature. Repulsive coulombic interactions between adjacent dithiadiazolyl radical cations may be responsible for preventing the spin-paired dimerisation process in [p-SNSNC–C$_6$H$_4$–CNSSN]Cl although there would appear to be ample scope for intramolecular spin–charge separation. At temperatures below 100 K, Curie–Weiss behaviour is observed with $\theta = -11$ K and an increased effective moment of 2.6. This may represent a structural phase transition.

Differential Scanning Calorimetry.—The DSC measurements on a variety of 1,3,2,4-dithiadiazol-yl/ylium ring systems has shown that, in some cases, thermolysis leads to solid-state rearrangement from the 1,3,2,4 to the 1,2,3,5 isomer.[1c] Such rearrangement has been attributed to secondary interactions in the solid state which facilitate rearrangement through a head-to-tail interaction between dithiadiazolyl rings.[1c] The DSC measurements on the radical cation [p-SNSNC–C$_6$H$_4$–CNSSN]Cl show an exothermic decomposition (280 °C) to leave a brown tar. There was no evidence for a possible rearrangement product. Both CV and ESR data indicated the presence of a cationic 1,3,2,4-dithiadiazolylium ring and a neutral 1,2,3,5-dithiadiazolyl radical and this is supported by these DSC data (no rearrangement of 1,3,2,4-dithiadiazolylium chlorides has been observed to date although the iodides do show rearrangement exotherms at elevated temperatures[1c]). Since the radical cation salt [SNSNC–C$_6$H$_4$–CNSSN]Cl is paramagnetic in the solid state, then the type of molecular packing can be considered to be determined largely by coulombic cation–anion interaction terms rather than the spin-paired 1,2,3,5-dithiadiazolyl dimerisation process. This is not unexpected since the energy of dimerisation is low, whereas lattice-energy terms tend to be high.

The DSC measurements on the mixed diradical, [p-SNSNC–C$_6$H$_4$–CNSSN]$^{2\cdot}$, also show an exothermic decomposition (261.5 °C) to leave an oily tar. On the basis of our previous proposals for solid-state rearrangement[1c] we may infer that although the 1,3,2,4-dithiadiazolyl rings are held together through a spin-paired interaction (p-SNSNC–C$_6$H$_4$–CNSSN is very weakly paramagnetic in the solid state) it does not involve a head-to-tail arrangement. We may thus consider an alternative structure, such as that shown below, in which the structure is determined through the head-to-head dimerisation of 1,2,3,5-dithiadiazolyl radicals leading to a similar head-to-head arrangement of 1,3,2,4-dithiadiazolyl rings. Such a structure would not facilitate such rearrangement, but would allow the required spin-paired interactions which make this material only weakly paramagnetic.

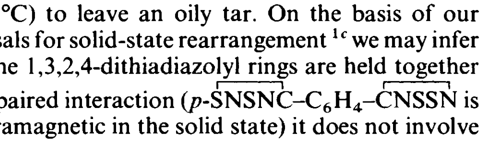


Table 3 Atomic coordinates (× 10^4) for [p-SNSNC–C_6H_4–CNSSN]-[AsF_6]$_2$·MeCN

Atom	*x*	*y*	*z*
S(1)	6984(3)	5110(2)	1056.1(15)
S(2)	7060(3)	3553(2)	1330(2)
S(3)	5500(3)	7089.8(15)	6583.0(14)
S(4)	5267(3)	8067.8(14)	5813.0(14)
N(1)	7175(9)	4238(5)	640(5)
N(2)	6732(9)	4014(4)	2201(5)
N(3)	5779(9)	6491(4)	5819(4)
N(4)	5516(9)	7609(4)	4931(4)
C(1)	6658(10)	4793(6)	2104(5)
C(2)	5768(10)	6815(5)	5020(5)
C(3)	6408(11)	5331(5)	2836(5)
C(4)	6797(11)	5072(6)	3675(6)
C(5)	6613(11)	5553(6)	4380(5)
C(6)	5953(10)	6318(5)	4249(5)
C(7)	5520(10)	6577(5)	3409(5)
C(8)	5741(11)	6086(5)	2704(5)
As(1)	523.8(12)	7217.8(6)	5759.9(6)
F(11)	−218(8)	6278(3)	5893(5)
F(12)	−478(8)	7236(4)	4751(3)
F(13)	−1126(6)	7616(4)	6208(4)
F(14)	1520(7)	7200(4)	6776(3)
F(15)	2200(6)	6815(4)	5331(4)
F(16)	1278(7)	8157(3)	5627(4)
As(2)	8013.5(11)	5678.8(6)	8517.8(6)
F(21)	6949(6)	5636(4)	7518(3)
F(22A)	8507(48)	4694(7)	8558(15)
F(23A)	6345(18)	5449(23)	9059(13)
F(24A)	7484(50)	6662(8)	8553(16)
F(25A)	9771(15)	5878(26)	8055(13)
F(22B)	7503(32)	4694(6)	8595(12)
F(23B)	6259(13)	5900(16)	8977(13)
F(24B)	8538(35)	6645(7)	8371(12)
F(25B)	9682(14)	5366(18)	8026(11)
F(26)	9065(6)	5720(3)	9522(3)
N(5)	4974(12)	8397(6)	7593(6)
C(9)	5485(13)	8830(6)	8101(6)
C(10)	6211(13)	9401(6)	8736(7)

Conclusion

N-Lithio complexes Li[RC(NSiMe$_3$)$_2$] {formed by reaction of RCN with 1 equivalent of Li[N(SiMe$_3$)$_2$]} react with SCl_2 to form substituted dithiadiazolylium salts [RCNSSN]Cl. This route to dithiadiazolylium salts is particularly advantageous in cases where the persilylated amidine precursors cannot be formed, particularly *m*- and *p*-NCC_6H_4C(=NSiMe$_3$)N(SiMe$_3$)$_2$. Metathesis of [*m*- or [*p*-NCC_6H_4CNSSN]Cl, formed in this manner, with Ag[AsF_6] gave the corresponding hexafluoroarsenate(V)] salts which reacted with [SNS][AsF_6] to form the mixed dithiadiazolylium salts [*m*- and [*p*-SNSNC–C_6H_4–CNSSN][AsF_6]$_2$. Partial and complete reduction of these salts led to the isolation of the analogous radical cations and diradicals. In comparison with other solid-state dithiadiazolyl radicals, the radical cation salt [*p*-SNSNC–C_6H_4–CNSSN]Cl is strongly paramagnetic in the solid state. Work is now in progress to enhance the secondary interactions between radical sites through (*i*) an increase in spin multiplicity, (*ii*) the preparation of selenium derivatives of these materials and (*iii*) the formation of different salts of these radical cations; the type of molecular packing observed for $S_3N_3^-$ salts is significantly different from those observed for AsF_6^- or Cl^- salts.

Experimental

General Procedures.—All reactions and manipulations were carried out under an atmosphere of dry nitrogen, using standard double-manifold techniques and a glove-box (Vacuum Atmospheres Corporation HE43-2 fitted with an HE 493 Dri-Train). Solvents were distilled, dried and degassed before use. Infrared spectra were recorded as Nujol mulls between KBr or CsI plates using a Perkin Elmer 577 grating spectrophotometer, ^{1}H NMR spectra on a Varian 400 MHz spectrometer and ESR spectra on a Varian V-4502 spectrometer. The C, H and N analyses were carried out using a Carlo-Erba elemental analyser.

Cyclic voltammograms were recorded using a Ag–Ag$^+$ reference electrode[24] (calibrated with reference to the standard calomel electrode), a potential-wave generator (type CV-1B; Bioanalytical Systems, W. Lafayette, IN) and a Linseis x-y chart recorder (type LY 17100). Solutions (*ca.* 0.001 mol dm^{-3}) of the electroactive species were prepared in MeCN and 0.1 mol dm^{-3} [NBu$_4$][BF$_4$] was used as the supporting electrolyte.

Starting Materials.—The salt [SNS][AsF_6] was prepared according to the literature method[25] with some modifications,[1b] $C_6H_4(CN)_2$-*m* -*p* (Aldrich) was sublimed *in vacuo* prior to use, [NBu$_4$]Cl was precipitated twice from acetone with diethyl ether and baked *in vacuo* and Ag[AsF_6], Li[N(SiMe$_3$)$_2$], SbPh$_3$ (Aldrich), [NBu$_4$][BF$_4$] (electrochemistry grade, Fluka) and SCl_2 (Fluka) were used without further purification.

Preparations.—[NCC_6H_4CNSSN]Cl. The salt Li[N(SiMe$_3$)$_2$] (13 g, 0.078 mol) and $C_6H_4(CN)_2$ (10 g, 0.078 mol) were stirred in Et_2O (40 cm^3) at room temperature for 18 h and then pumped to dryness to provide an off-white solid. This solid was slowly added to a solution of SCl_2 (10 cm^3, 0.155 mol) in CH_2Cl_2 (50 cm^3) with cooling on an ice-bath to form an immediate orange precipitate which was filtered off and pumped to dryness. The crude product was then extracted with SO_2 in a sealed extractor[26] and washed liberally with CH_2Cl_2.

[*p*-NCC_6H_4CNSSN]Cl: yield 13.5 g, 72%. IR: ν_{max} 2220m, 1285w, 1212w, 1150s, 1012m, 920m, 890s, 857s, 850s, 837 (sh), 740s, 720w, 685s, 552s, 520w, 455w and 405w cm^{-1}. Mass spectrum (electron impact, positive ion mode, EI$^+$): *m*/*z* 205.86 (81.32), 159.92 (28.38), 127.97 (25.63), 101.98 (14.28), 100.97 (13.98), 77.91 (100.00), 74.98 (13.44), 49.99 (13.05), 45.95 (22.56%) (Found: C, 39.10; H, 1.70; N, 17.20. Calc.: C, 39.75, H, 1.65; N, 17.40%).

[*m*-NCC_6H_4CNSSN]Cl: yield 13.1 g, 70%. IR: ν_{max} 2232m, 1670m, 1307m, 1234m, 1206m, 1177m, 1136m, 1092m, 1000m, 969m, 910m, 895s (sh), 890s, 857s, 850m, 816s, 796m, 720m (sh), 716vs, 680m, 590m (sh), 583m, 565m, 535m, 515w, 473w, 457w, 414w, 388w, 315m, 310w (sh) and 297w cm^{-1} (Found: C, 39.55; H, 1.60; N, 16.90. Calc.: C, 39.75; H, 1.65; N, 17.40%).

[NCC_6H_4CNSSN][AsF_6]. The salt [NCC_6H_4CNSSN]Cl (1.21 g, 5.0 mmol) and Ag[AsF_6] (1.50 g, 5.1 mmol) were placed in one limb of a two-limbed reaction vessel and liquid SO_2 was condensed on. The reagents were stirred for 16 h at room temperature during which time a yellow-white precipitate formed under a yellow solution. The soluble material was filtered off and the residues washed with back-condensed liquid SO_2 to give a residual white powder (AgCl) and a yellow solid after evaporation to dryness.

[*p*-NCC_6H_4CNSSN][AsF_6]: yield 1.78 g, 90%. IR: ν_{max} 2244s, 1653w (sh), 1607m, 1507w, 1445m (sh), 1399vs, 1377vs, 1342w (sh), 1333w (sh), 1300w, 1285m, 1204m, 1182m, 1161m, 1018m, 938w, 921m, 852m, 849m, 814m, 703vs, 688vs (sh), 677vs (br), 617w, 574vw (sh), 562m, 553m, 542w (sh), 524vw and 398vs (Found: C, 24.30; H, 1.25; As, 18.65; N, 10.60. Calc.: 24.30; H, 1.00; As, 18.75; N, 10.65%).

[*m*-NCC_6H_4CNSSN][AsF_6]: yield 1.90 g, 96%. IR: ν_{max} 2260s, 1685m, 1606m, 1585vw, 1444vs, 1394vs, 1329vs, 1315w (sh), 1214m, 1181m, 1146m, 1095m, 1058m, 999vw, 983m, 965w, 928m, 918m, 861m, 820m (sh), 813m, 810w (sh), 798m, 696m (sh), 677vs (br), 588m, 567m, 552m, 507vw, 480w, 462w and 398vs cm^{-1} (Found: C, 24.20; H, 1.25; As, 18.90; N, 10.50. Calc.: C, 24.30; H, 1.00; As, 18.75; N, 10.65%).

$[NCC_6H_4CNSSN]_2$. The salt $[NCC_6H_4CNSSN]Cl$ (1.00 g, 4.1 mmol) and $SbPh_3$ (0.73 g, 2.1 mmol) were placed in a Schlenk tube and MeCN (15 cm^3) added. The mixture was stirred for 16 h, filtered and the maroon product washed with MeCN (4 × 5 cm^3) before exhaustive extraction with CH_2Cl_2 in a sealed extractor.[26]

[*p*-$NCC_6H_4CNSSN]_2$: yield 780 mg, 91%. IR: ν_{max} 2222s, 1605s, 1438s (sh), 1415s, 1362vs, 1310m, 1262s, 1195w (sh), 1188m, 1170s, 1135s, 1103m, 1015m, 998w, 905w, 890vw, 848vs, 832vs, 816s, 788vs, 747w, 728m, 680w, 647m, 642m (sh), 532s, 500s, 440m, 430m and 390 cm^{-1} (Found: C, 46.90; H, 1.90; N, 20.00. Calc.: C, 46.60; H, 1.95; N, 20.35%).

[*m*-$NCC_6H_4CNSSN]_2$: yield 740 mg, 87%. IR: ν_{max} 2230s, 1438s (sh), 1365s (sh), 1315m, 1298m, 1264m, 1208m, 1202m, 1180m, 1172m, 1130m, 1120m, 1102m, 1098m (sh), 1022w, 1000w, 990w, 955m, 938m, 930w, 918w, 905s, 842vs, 840m (sh), 814vw, 809vs, 795vs, 777vs (br), 750w, 735m, 727m (sh), 700w (sh), 687vs, 673w, 669w, 570s, 562s, 512s, 480m, 455m, 445m, 390vs and 385vw cm^{-1} (Found: C, 46.80; H, 1.90; N, 20.35. Calc.: C, 46.60; H, 1.95; N, 20.35%).

$[SNSNC{-}C_6H_4{-}CNSSN][AsF_6]_2$. The salt $[SNS][AsF_6]$ (0.680 g, 2.5 mmol) and $[NCC_6H_4CNSSN][AsF_6]$ (1 g, 2.5 mmol) were placed in one limb of a two-limbed reaction vessel and liquid SO_2 condensed on. The reagents were stirred at room temperature for 18 h during which time a pale yellow precipitate formed under a red solution. The soluble material was filtered off and the solid product washed with back-condensed SO_2 and then with CH_2Cl_2.

[*p*-$SNSNC{-}C_6H_4{-}CNSSN][AsF_6]_2$: yield 1.630 g, 97%. IR: ν_{max} 1518m, 1400s, 1302w, 1205w, 1162m, 1020w, 990s, 922s, 888w, 852s, 845m, 832w, 800s, 749m, 700vs, 670s, 630w, 590w, 560w, 440w and 400s cm^{-1} (Found: C, 14.55; H, 0.65; As, 22.75; N, 8.50. Calc.: C, 14.50; H, 0.60; As, 22.65; N, 8.45%). ^1H NMR (CD_3CN): δ 8.46 (m, 1 H), 8.44 (m, 1 H), 8.27 (m, 1 H) and 8.25 (m, 1 H).

[*m*-$SNSNC{-}C_6H_4{-}CNSSN][AsF_6]_2$: yield 1.240 g, 94%. IR: ν_{max} 1772w, 1689m, 1654w, 1607m, 1582w, 1488m (sh), 1410m (sh), 1393vs, 1332w (sh), 1301w (sh), 1219m, 1181w, 1149m, 1118vw, 1094vw, 1030vw, 1009m, 998vw (sh), 983w (sh), 970m, 926m, 919m (sh), 894m (sh), 885m, 861w, 849m, 823m, 814m, 799s, 701vs (br), 676m (sh), 640m (sh), 586m, 578m, 562m, 527vw, 455vw, 436w and 398vs (br) cm^{-1} (Found: C, 14.90; H, 0.70; As, 22.70; N, 8.45. Calc.: C, 14.50; H, 0.60; As, 22.65; N, 8.45%).

$[SNSNC{-}C_6H_4{-}CNSSN]Cl_2$. The salt $[SNSNC{-}C_6H_4{-}CNSSN][AsF_6]_2$ (1.00 g, 1.5 mmol) and NBu_4Cl (1.00 g, 3.4 mmol) were placed in one limb of a two-limbed reaction vessel and MeCN (5 cm^3) added against a counterflow of nitrogen. The mixture was stirred for 18 h during which time a pale orange solid formed under an orange-yellow solution. The soluble material was filtered off and the orange, residual product washed three times with back-condensed acetonitrile to yield a fine orange powder.

[*p*-$SNSNC{-}C_6H_4{-}CNSSN]Cl_2$: yield 0.500 g, 94%. IR: ν_{max} 1682w, 1599vw, 1528vw, 1509w, 1428m, 1388vs, 1300m, 1214w, 1154w, 1120m, 1015m, 978m, 923m, 891m, 852m, 780w, 745m, 723w, 701w, 685m, 668w, 621w, 579w, 545w and 421m cm^{-1}. Mass spectrum (EI^+): *m/z* 283.69 (45.88), 237.75 (19.12), 205.81 (77.55), 159.87 (27.14), 127.92 (57.82), 101.95 (18.05), 100.94 (20.83), 77.88 (100.00), 63.89 (46.84), 49.97 (19.12) and 45.94 (25.49%) (Found: C, 27.35; H, 1.15; N, 15.30. Calc.: C, 27.05; H, 1.15; N, 15.75%).

[*m*-$SNSNC{-}C_6H_4{-}CNSSN]Cl_2$: yield 0.440 g, 83%. IR: ν_{max} 1680m, 1510vs (br), 1420m, 1295m, 1220m, 1145w, 1090m, 1000m, 948m, 905m (sh), 985m, 875m, 850m, 820m, 792m, 715vs, 675m, 652w, 627m, 576m (sh), 572m, 551m and 420m (br) cm^{-1}. (Found: C, 27.35; H, 1.50; N, 15.75. Calc.: C, 27.05; H, 1.15; N, 15.75%).

$[SNSNC{-}C_6H_4{-}CNSSN]$. The salt $[SNSNC{-}C_6H_4{-}CNSSN]Cl_2$ (300 mg, 0.85 mmol) and $SbPh_3$ (300 mg, 0.85 mmol) were placed in one limb of a two-limbed reaction vessel and CH_2Cl_2 (5 cm^3) added. The mixture was stirred in the dark for 16 h, filtered and the grey-green product washed with back-condensed CH_2Cl_2 (3 × 5 cm^3).

[*p*-$SNSNC{-}C_6H_4{-}CNSSN]$: yield 210 mg, 78%. IR: ν_{max} 1516m, 1413s, 1099s, 937m, 903w, 851w, 833w, 804m, 782m, 723m, 648w, 594w, 510m and 460m cm^{-1} (Found: C, 33.55; H, 1.50; N, 19.90. Calc.: C, 33.80; H, 1.40; N, 19.70%).

[*m*-$SNSNC{-}C_6H_4{-}CNSSN]$: yield 115 mg, 43%. IR: ν_{max} 1679s (br), 1503m, 1409vs, 1286m, 1233s, 1202s, 1102s, 1020s, 896w, 849w, 830w, 804m, 797m, 785m, 722s, 708m, 693m, 680m, 615w, 602vw, 513vw, 456vw and 413vw cm^{-1} (Found: C, 31.75; H, 1.50; N, 19.75. Calc.: C, 33.80; H, 1.40; N, 19.70%).

$[SNSNC{-}C_6H_4{-}CNSSN]Cl$. The salt $[SNSNC{-}C_6H_4{-}CNSSN]Cl_2$ (375 mg, 1.1 mmol) and $SbPh_3$ (186 mg, 0.05 mmol) were placed in one limb of a two-limbed reaction vessel and CH_2Cl_2 (5 cm^3) added. The mixture was stirred in the dark for 2 h, filtered and the insoluble product washed with back-condensed CH_2Cl_2 (4 × 5 cm^3).

[*p*-$SNSNC{-}C_6H_4{-}CNSSN]Cl$: yield 300 mg, 89%. IR: ν_{max} 1772w, 1689m, 1654w, 1607m, 1582w, 1488m (sh), 1410m (sh), 1393vs, 1332w (sh), 1301w (sh), 1219m, 1181s, 1149m, 1118vw, 1094vw, 1030vw, 1009m, 998vw (sh), 984m (sh), 885m, 861w, 849m, 823m, 814m, 799s, 701s (br), 676m (sh), 640m (sh), 586m, 562m, 527vw, 455vw, 436w and 398vs (br) cm^{-1} (Found: C, 30.50; H, 1.55; N, 17.65. Calc.: C, 30.05; H, 1.25; N, 17.55%).

[*m*-$SNSNC{-}C_6H_4{-}CNSSN]Cl$: yield 52 mg, 77%. IR: ν_{max} 1778m, 1728w, 1698w, 1687m, 1678w, 1666w, 1620vw, 1600w, 1530w, 1403vs, 1302w, 1114s, 773m, 722m, 618m, 578w, 511w, 421m and 401w cm^{-1} (Found: C, 30.05; H, 1.90; N, 17.50. Calc.: C, 30.05; H, 1.25; N, 17.55%).

X-Ray Crystallography for [*p*-$SNSNC{-}C_6H_4{-}CNSSN][AsF_6]_2{\cdot}MeCN$.—*Crystal data.* $C_{10}H_7As_2F_{12}N_5S_4$, M = 703.29, monoclinic, space group $P2_1/n$, a = 8.233(3), b = 16.742(6), c = 15.332(7) Å, β = 94.21(5)°, U = 2107.6(14) $Å^3$, Z = 4, D_c = 2.216 g cm^{-3}, λ(Cu-Kα) = 1.541 78 Å, μ = 8.769 mm^{-1}, $F(000)$ = 1360.

Data collection and processing. A crystal of size 0.50 × 0.05 × 0.05 mm was examined on a Stoe-Siemens diffractometer equipped with Cryostream cooler;[27] all measurements were made at 170 K. Cell parameters were refined from θ values (11.63–17.31°) of 32 reflections measured at $\pm\omega$. Data collection employed a ω–θ scan mode with on-line profile fitting,[28] $2\theta_{max}$ = 110°, index ranges $-8 \leqslant h \leqslant 8$, $-5 \leqslant k \leqslant 17$, $-3 \leqslant l \leqslant 16$. No significant variation in intensities of three standard reflections was observed. Semiempirical absorption corrections were applied based on sets of equivalent reflections measured at a range of azimuthal angles;[29] transmission factors were in the range 0.114–0.227. Of 3374 reflections measured, 2633 were unique (R_{int} = 0.050) and 1715 had $I > 2\sigma(I)$.

Structure determination.[29] Structure solution was by direct methods. Full-matrix least-squares refinement on F^2 used all the data and a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0825P)^2$, where $P = (F_o^2 + 2F_c^2)/3$. 312 Parameters were refined, including anisotropic displacement parameters and two-fold rotational disorder for one of the anions [relative occupancy 54:46(4)%; only one component is shown in Fig. 2]; As–F bond lengths were restrained to be approximately equal, and constraints were applied to displacement components of some *trans* pairs of fluorine atoms to assist in the disorder refinement. Hydrogen atoms were constrained. The final conventional R calculated on F for observed data only was 0.0479, and the weighted F^2 discrepancy factor on all data was 0.1496, with a goodness of fit of 1.057. A final difference synthesis showed no features outside the range ±0.9 e Å^{-3}; the largest features were close to the disordered anion. Atomic scattering factors were inbuilt in the refinement program. Atomic coordinates are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We thank the SERC for two post-doctoral research assistantships (to J. M. R. and R. J. W.), a research studentship (to I. L.) and a research grant (to W. C.), and the Royal Society for an equipment grant (to W. C.).

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Received 5th *October* 1992; *Paper* 2/05325J