Preparation of Salts of the 5,5′-(1,4-Phenylene)bis(1,3,2,4-dithiadiazolylium) Dication and of its 1,2- and 1,3-Phenylene Analogues. Preparation and Crystal Structure of the Stacked, Neutral 5,5′-(1,4-Phenylene)bis(1,3,2,4-dithiadiazole)†

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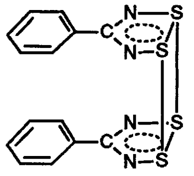
Reactions of *o*-, *m*- and *p*-$C_6H_4(CN)_2$ with [SNS][AsF_6] in liquid SO_2 produced the AsF_6^- salts of *o*-, *m*- and *p*-$[C_6H_4(CNSNS)_2]^{2+}$ in high yield. The *para*-phenylene AsF_6^- salt was readily converted (>75%) into other salts (Cl^-, Br^-, $SbCl_6^-$ or $S_3N_3^-$) by anion metathesis. Reduction of [*p*-C_6H_4-$(CNSNS)_2]Cl_2$ with $SbPh_3$ gave the bis(dithiadiazole), *p*-$C_6H_4(CNSNS)_2$, which crystallises in the triclinic space group $P\bar{1}$, with $a = 5.772(1)$, $b = 6.382(1)$, $c = 7.491(1)$ Å, $\alpha = 79.21(1)$, $\beta = 82.86(1)$, $\gamma = 70.25(1)°$, $Z = 1$; $R = 0.077$ for 678 observed reflections. The structure shows equidistant molecular stacking of the *trans* isomer with weak S···S (3.214 Å) and S···N (3.346 Å) intermolecular interactions.

The relatively little investigated 1,2,3,5-dithiadiazole free radicals, which are found associated in the solid state, *e.g.* **I**,[1] undergo a variety of unusual reactions. For instance, **I** reacts with zero-valent metal species to give free-radical metal complexes such as $[Fe_2(CO)_6(PhCNSSN)]$[2] and $[Ni_2(C_5H_5)_2$-$(PhCNSSN)]$.[3] They have also been found to produce a variety of salts, *e.g.* $[CF_3CNSSN]_3Cl$[4] and $[PhCNSSN]_2Cl$,[5] which contain two or more interacting CN_2S_2 rings with the heterocycle possessing a fractional oxidation state.



I

Thus 1,2,3,5-dithiadiazolylium cations can readily accept some partial charge and their corresponding dithiadiazoles can be expected to form charge-transfer complexes. This was confirmed recently[5] by the isolation of $[PhCNSSN][S_3N_3]$ (Fig. 1), prepared from either ionic or free-radical precursors.[5] *Ab initio* calculations indicated ionic charges of only +0.14 and −0.14 on the PhCNSSN and S_3N_3 rings respectively. Similar secondary interactions have been observed in other materials[5] such as $[PhCNSSN][S_3N_2]Cl$ (Fig. 2) and $[(PhCNSSN)_2Cl]$-$[S_3N_3]$.

In order to increase these secondary interactions further, we have attempted the synthesis of some bis-, tris- and poly-dithiadiazole/ylium species, the higher symmetry of these materials leading hopefully to more highly ordered solid-state structures, *c.f.* ref. 6.

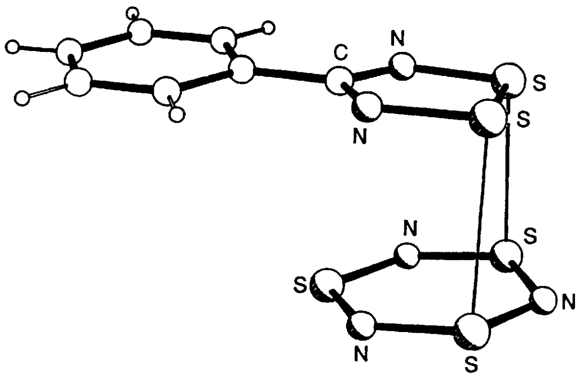


Fig. 1 4-Phenyl-1,2,3,5-dithiadiazolylium-1,3,5,2,4,6-trithiatriazinide, showing S···S secondary interactions (2.864 and 2.812 Å)

Results and Discussion

In an initial attempt to prepare a bis(dithiadiazolylium) compound, 1,4-dicyanobenzene was treated with $(NSCl)_3$ [formed *in situ* according to the general method shown in Scheme 1(*a*)]. However, this produced only small quantities (1–2%) of impure monosubstituted product, $[NCC_6H_4$-$CNSSN]Cl$.[7]

Consequently we turned to the SNS^+ synthon which is known to produce good yields of the 1,3,2,4-isomeric ring[8–10] [Scheme 1(*b*)]. Reduction of these 1,3,2,4-dithiadiazolylium rings has previously been shown to be a convenient route to the 1,2,3,5-dithiadiazole species *via* a photochemically allowed isomerisation process.[8]

Reaction of poorly soluble $[SNS][SbCl_6]$[11] with *p*-$C_6H_4(CN)_2$ in refluxing CH_2Cl_2 yielded only a variety of intractable products, but in contrast the room-temperature reaction of $[SNS][AsF_6]$[12] with *o*-, *m*- or *p*-$C_6H_4(CN)_2$ in liquid SO_2 gave the required salts in high yield as shown in Scheme 2.

In an analogous manner the 1,3,5-tris(dithiadiazolylium) benzene species has also been prepared in 80% yield; the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: eV ≈ 1.6 × 10^{-19} J, G = 10^{-4} T.

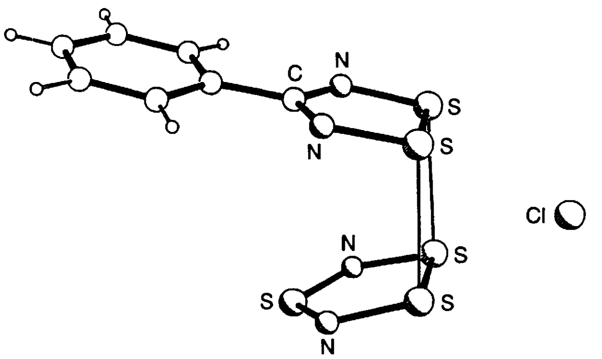
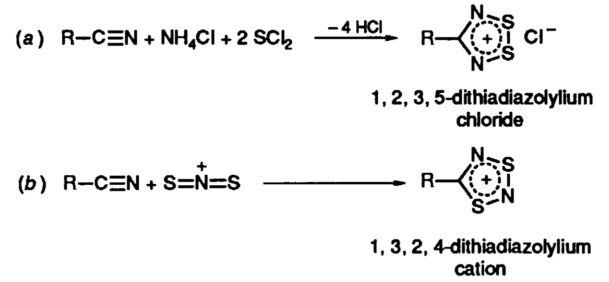
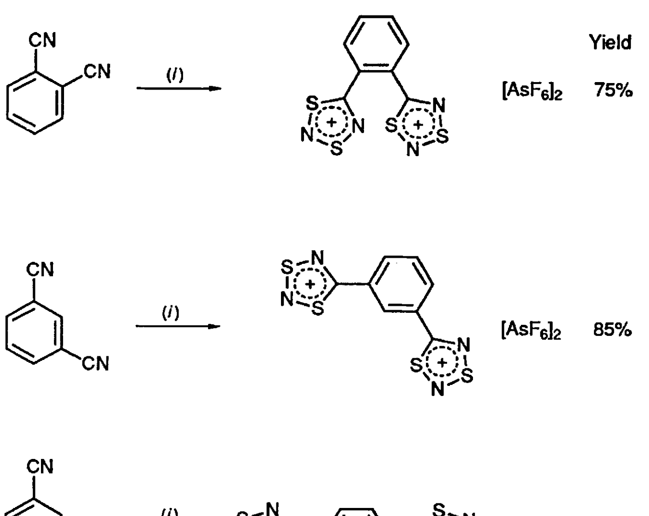


Fig. 2 4-Phenyl-1,2,3,5-dithiadiazolylium-1,2,4,3,5-trithiadiazole chloride, showing the weak S • • • S secondary interactions between the rings (2.876 and 2.935 Å)



Scheme 1 The two isomeric dithiadiazolylium cations

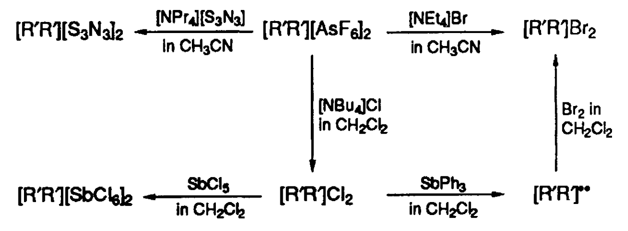


Scheme 2 Reaction of [SNS][AsF_6] with *o*-, *m*- and *p*-$C_6H_4(CN)_2$. (*i*) 2[SNS][AsF_6], liquid SO_2

chemistry and reactivity of this species will be discussed more fully in a forthcoming publication.[13]

Compared with the *ortho*- and *meta*-dications (as AsF_6^- salts), the *para*-disubstituted analogue would appear to have a superior lattice stabilisation as indicated by an appreciably lower solubility in polar organic and inorganic solvents (CH_3CN, CH_2Cl_2 or SO_2), a higher thermal stability and a superior stability to hydrolysis. In the atmosphere, [*p*-$C_6H_4(CNSNS)_2$][AsF_6]$_2$ is only slightly hydrolysed even after several days whereas the *ortho*- and *meta*-analogues are largely decomposed within a few hours.

Metathesis reactions of 1,4-phenylenebis(1′,3′,2′,4′-dithiadiazolylium) hexafluoroarsenate(V) with a variety of tetra-alkylammonium salts produced other salts in high yield (> 75% isolation), as shown in Scheme 3.



Scheme 3 Reactions of the 1,4-phenylenebis(1′,3′,2′,4′)-dithiadiazolylium cation (R′R′)

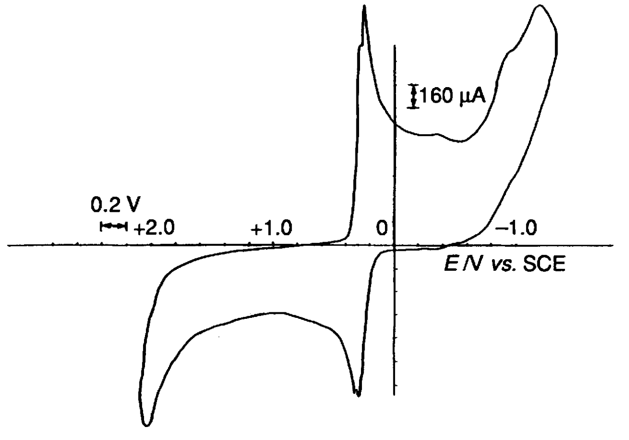


Fig. 3 Cyclic voltammogram at −20 °C of [*p*-$C_6H_4(CNSNS)_2$][AsF_6]$_2$ in CH_3CN using [NBu_4][AsF_6] as supporting electrolyte; $E_{\frac{1}{2}}$(red.) = 0.224 V

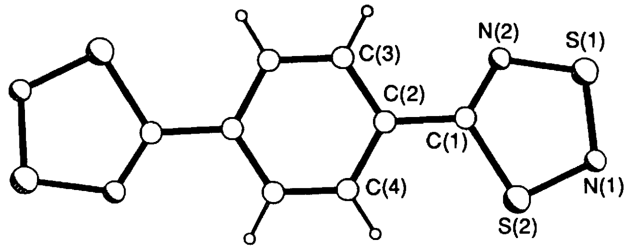


Fig. 4 5,5′-(1,4-Phenylene)bis(1,3,2,4-dithiadiazole) showing the atom numbering

Cyclic Voltammetry.—Cyclic voltammetry (Fig. 3) of the *para*-dication showed reversible reduction, *via* an intermediate radical cation, to give a neutral product. However, the two reduction (and corresponding oxidation) peaks are only just resolvable. Consequently it was not surprising that the isolation of the intermediate radical cation, [*p*-$C_6H_4(CNSNS)_2$]$^{\bullet+}$, on a preparative scale by a variety of methods [partial chemical reduction or *via* reaction of a 1:1 mixture of the dication and neutral bis(dithiadiazole)] was unsuccessful; only mixtures of *p*-$C_6H_4(CNSNS)_2$ and [*p*-$C_6H_4(CNSNS)_2$][AsF_6]$_2$ were obtained.

Chemical reduction of the *para*-dication dichloride with triphenylantimony gave the expected bis(dithiadiazole), *p*-$C_6H_4(CNSNS)_2$, as a black microcrystalline powder. Longer needles suitable for an X-ray crystallographic study were obtained by slow diffusion.

Structure.—The molecular structure of *p*-$C_6H_4(CNSNS)_2$ is shown in Fig. 4. The molecule lies on a crystallographic inversion centre. It is essentially planar: each dithiadiazole ring

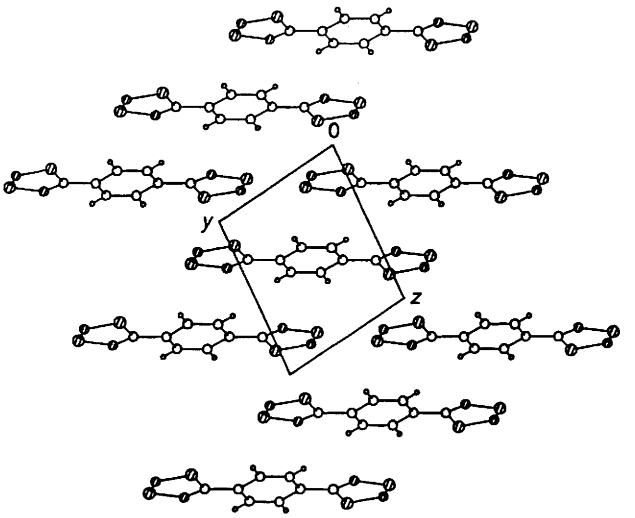


Fig. 5 Unit cell packing of 5,5′-(1,4-phenylene)bis(1,3,2,4-dithiadiazole)

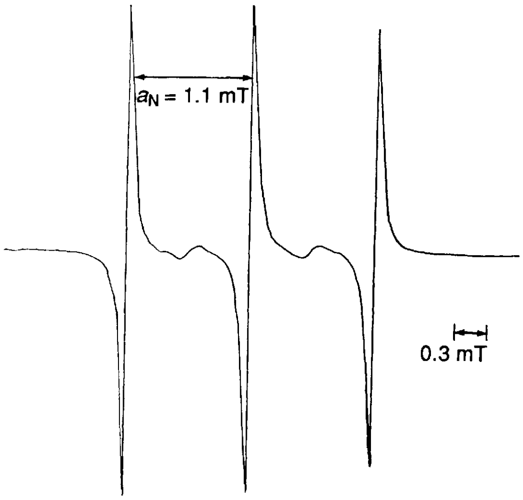


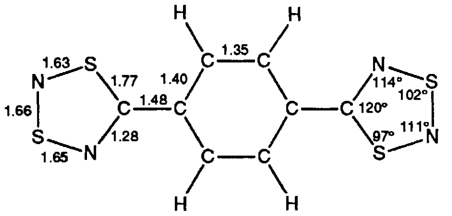
Fig. 6 ESR spectrum of p-$C_6H_4(\overline{CNSNS})_2$ in tetrahydrofuran

[root mean square (r.m.s.) $\Delta = 0.038$ Å] has a dihedral angle of 5.4° to the central phenylene ring (r.m.s. $\Delta = 0.004$ Å), and most of this departure from coplanarity of the rings consists of a twist about the C–C bond [mean torsion angle for S(2)–C(1)–C(2)–C(4) and N(2)–C(1)–C(2)–C(3) is −4.1°], with only a very small degree of folding perpendicular to this bond.

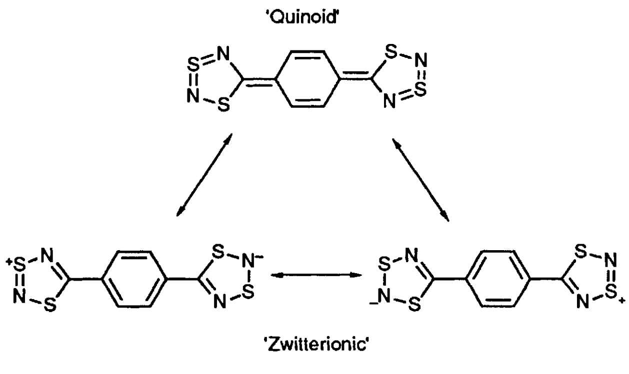
The crystal structure shows a parallel packing of molecules which are slipped along the long axis so that each molecule overlaps several others (Fig. 5). The secondary interactions, between the outermost SN bonds of adjacent molecules [d(N···S) = 3.11 Å, d(S···S) = 3.21 Å], though weak, appear to be responsible for holding the molecules in a polymeric array. This can be deduced using data produced by Nyburg and Faerman.[14] Although their paper deals exclusively with atoms bonded terminally to carbon by multiple bonds, we can use their ideas, principally that the van der Waals radius of an atom is not spherically constant, but is probably rather smaller along the line of bonds to that atom; certainly this is the case for sulphur. If we take the values proposed in this paper, possibly significant contact distances will be those less than 3.20 Å for N···N and the limits for N···S and S···S will be in the ranges 3.20–3.63 (N···S) and 3.20–4.06 Å (S···S), depending on the orientation of the contact vector relative to the bonds.

In the light of this, the shortest N···N, N···S and S···S distances in p-$C_6H_4(\overline{CNSNS})_2$ fall into two classes. First there are those interactions which are approximately coplanar with the molecules. The shortest of these distances are N···N 3.227, N···S 3.111 and S···S 3.702 Å and judging by the above criteria, it would appear that these are probably very weak interactions.

Secondly, by contrast, there are short contacts between parallel CN_2S_2 rings, particularly S···S at 3.214 and S···N at 3.346 Å. In Fig. 5, there are, for example, interactions between the two rings on either side of the letter y. These definitely appear to be significant, and they link molecules together into one-dimensional polymeric chains, the 'right-hand end' of each molecule overlapping with the 'left-hand end' of the next one (in Fig. 5, consider the interactions through the letters y and z, linking three molecules together in this way to form part of such a chain). Thus the packing and secondary interactions are such as to produce an evenly spaced, though slipped, molecular stack with one molecule per unit cell.



Approximate bond distances (Å) and angles (°) (as shown above) derived from the crystal data indicate that a simple understanding of the structure can be made (according to valence bond theory) *viz.* several zwitterionic forms combining with a quinoid contribution to provide an electron-paired molecule. The uneven C–C distances in the central ring and the shortened C–C distance between rings (1.48 compared with 1.52 Å in biphenyl)[15] show that the quinoid form makes a significant contribution to the overall structure.



Samples of p-$C_6H_4(\overline{CNSNS})_2$ were, however, found to be ESR-active in both the powdered solid state and in solution (Fig. 6) showing a simple 1:1:1 triplet hyperfine structure corresponding to strong localisation of the unpaired electron spins on the remote nitrogen atoms. Consequently a purely valence-bond description of the bonding in p-$C_6H_4(\overline{CNSNS})_2$ is inadequate.

Semi-empirical PM3 molecular-orbital calculations on this molecule show that the triplet state is of lower energy than an electron-paired singlet state by some 3 eV. This triplet state contains a pair of essentially degenerate ($\Delta E < 0.1$ eV) frontier orbitals [(40) and (41)] (see Fig. 7). Thus it was not surprising to find that p-$C_6H_4(\overline{CNSNS})_2$ is strongly paramagnetic at room temperature.

Over a period of several days rearrangement of p-$C_6H_4(\overline{CNSNS})_2$ slowly occurred in tetrahydrofuran solution (in daylight at room temperature) to give the isomeric 1,2,3,5-

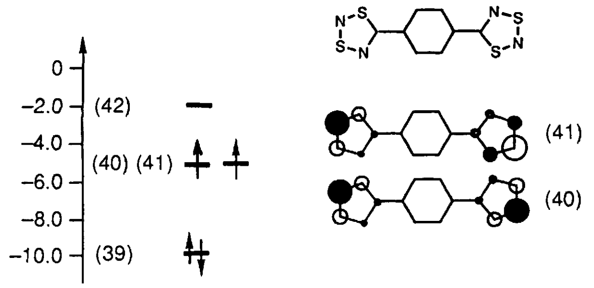


Fig. 7 Frontier orbitals of 5,5′-(1,4-phenylene)bis(1,3,2,4-dithiadiazole), according to PM3 molecular orbital calculations

Table 1 Analytical* data and yields for some bis(dithiadiazolylium) salts and for $p\text{-}C_6H_4(\overline{CNSNS})_2$

Compound	Yield (%)	Analysis (%) C	H	N
$[o\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$	75	14.5	0.6	8.5
		(14.5)	(0.6)	(8.5)
$[m\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$	85	14.3	0.5	8.4
		(14.5)	(0.6)	(8.5)
$[p\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$	92	14.6	0.6	8.1
		(14.5)	(0.6)	(8.5)
$[p\text{-}C_6H_4(\overline{CNSNS})_2]Cl_2$	85	26.8	1.2	15.9
		(27.0)	(1.1)	(15.8)
$[p\text{-}C_6H_4(\overline{CNSNS})_2]Br_2$	90	21.4	1.0	12.3
		(21.6)	(0.9)	(12.6)
$[p\text{-}C_6H_4(\overline{CNSNS})_2][S_3N_3]_2$	80	17.5	0.7	24.6
		(17.1)	(0.7)	(25.0)
$[p\text{-}C_6H_4(\overline{CNSNS})_2][SbCl_6]_2$	95	10.0	0.5	5.7
		(10.1)	(0.4)	(5.9)
$p\text{-}C_6H_4(\overline{CNSNS})_2$	90	33.6	1.5	9.5
		(33.8)	(1.4)	(9.7)

* Calculated values are given in parentheses.

bis(dithiadiazole) radical as indicated by a change in the ESR signal. In the solid state, however, the 1,3,2,4 isomer appears to be stable indefinitely to rearrangement. Further ESR studies are in progress.

During the course of this work, a more direct synthesis of $[p\text{-}C_6H_4(\overline{CNSSN})_2]Cl_2$ was achieved by Oakley and co-workers;[16,17] reduction of this chloride salt gave the neutral $p\text{-}C_6H_4(\overline{CNSSN})_2$ species.

Our isolation of a thermally and photochemically stable bis(1,3,2,4-diathiadiazole) analogue will enable an interesting comparison of the chemistry of these two isomeric rings to be made.

Conclusion

The synthesis of materials containing more than one dithiadiazolylium ring has been readily achieved by the reactions of $[SNS][AsF_6]$ with *o*-, *m*- and $p\text{-}C_6H_4(CN)_2$, the reactions occurring in high yields at ambient temperatures. The solubility properties of the various *para*-dication salts facilitated high yield metathesis reactions. Chemical reduction of the *para*-dication gave the corresponding neutral bis(dithiadiazole), the first dithiadiazole to form stacks in the solid state, a feature possibly induced by the higher degree of symmetry associated with these bis(dithiadiazoles).

Experimental

All reactions and manipulations were carried out under an atmosphere of dry nitrogen and solvents were dried before use. Infrared spectra were recorded as Nujol mulls between KBr or CsI plates using a Perkin-Elmer 577 or 457 grating spectrophotometer. Mass spectra were recorded by a VG Analytical 7070E spectrometer, ^1H NMR spectra at 250 MHz on a Brüker AM250 spectrometer and ESR spectra on a Varian V-4502 EPR spectrometer. Carbon, H and N analyses were carried out on a Carlo-Erba 1106 elemental analyser.

Materials.—The salt $[S_2N][AsF_6]$ was prepared according to the literature method,[12] $[NPr_4][S_3N_3]$ was prepared according to the literature method[18] with slight modifications.[19] The salts $[NBu_4]Cl$ and $[NEt_4]Br$ were precipitated twice from acetone by addition of diethyl ether, followed by baking (at 75 °C) *in vacuo*. The dicyanobenzenes (Aldrich) were recrystallised from acetone. The compounds $SbCl_5$ and $SbPh_3$ (Aldrich) were used without further purification (it was found that distillation or recrystallisation, respectively, of these starting materials had no noticeable effect on either yields or purity).

Preparations.—$[p\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$. The compound $p\text{-}C_6H_4(CN)_2$ (0.128 g, 1 mmol) was stirred with a slight excess of $[S_2N][AsF_6]$ (0.534 g, 2 mmol) in liquid SO_2 in a two-limbed reaction vessel for 18 h to yield an off-white precipitate under a rose solution. The volume was reduced and the crude product washed with minimal amounts of SO_2 and CH_2Cl_2 to remove coloured impurities. The product showed no ν(CN) IR absorption at *ca.* 2200 cm^{-1}. Yield: 0.609 g, 92%. IR: ν_{max}/cm^{-1} 1517s, 1435s, 1380s, 1350w, 1320w, 1297m, 1258w, 1227w, 1208w, 1170w, 1135mw, 1115w, 1030w, 1020w, 988s, 910m, 888w, 842ms, 820w, 803s, 770w, 700s br, 670m, 635s, 593m, 572m, 443ms and 400s. ^1H NMR (CD_3CN): δ 8.60s. MS [electron impact (EI)]: *m*/*z* 206 ($NCC_6H_4CN_2S_2$, 3.98), 128 (NCC_6H_4CN, 3.56), 104 (CN_2S_2, 1.54), 102 (C_6H_4CN, 1.14) and 76 (C_6H_4, 8.32%).

$[m\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$. As above but using $m\text{-}C_6H_4(CN)_2$ and $[S_2N][AsF_6]$ in the same amounts. The product showed no ν(CN) IR absorption at *ca.* 2200 cm^{-1}. Yield: 0.563 g, 85%. IR: ν_{max}/cm^{-1} 1600s, 1490m, 1420s, 1405s, 1340s, 1290m, 1250w, 1230w, 1195m, 1180m, 1150w, 1125w, 1045m, 1035s, 986s, 940m, 905m, 895s, 870m, 805m, 802s, 790m, 700s br, 635m, 620s, 590s, 575m and 525w. ^1H NMR (CD_3CN): δ 9.07 (t, 1 H), 8.74 (q, 2 H) and 8.16 (t, 1 H).

$[o\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$. As above but using $o\text{-}C_6H_4(CN)_2$ and $[S_2N][AsF_6]$ in the same amounts. The product showed no ν(CN) IR absorption at *ca.* 2200 cm^{-1}. Yield: 0.497 g, 75%. IR: ν_{max}/cm^{-1} 1585m, 1420s, 1405s, 1330s, 1220w, 1195m, 1170w, 1145s, 986s, 925m, 905m, 870m, 785s, 700s br, 585s, 570s, 530m, 450m and 400s. ^1H NMR (CD_3CN): δ 8.31 (m, 2 H) and 8.23 (m, 2 H).

$[p\text{-}C_6H_4(\overline{CNSNS})_2]Cl_2$. The salt $[p\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$ (0.662 g, 1 mmol) and a slight molar excess of $[NBu_4]Cl$ (0.555 g, 2 mmol) were stirred in CH_3CN to produce an instant lemon precipitate of $[p\text{-}C_6H_4(\overline{CNSNS})_2]Cl_2$. The product was filtered off and then extracted with CH_2Cl_2 in a sealed extractor.[20] Yield: 0.302 g, 85%. IR: ν_{max}/cm^{-1} 1510w, 1430m, 1293m, 1220w, 1110m br, 1020w, 970s, 910m, 860s, 840s, 805m, 777s, 720w, 660m, 630m, 575s, 420s and 405m. MS (EI): *m*/*z* 284 ($S_2N_2CC_6H_4CN_2S_2$, 11.3), 206 ($NCC_6H_4CN_2S_2$, 37.8), 160 (NCC_6H_4CNS, 11.4) and 128 (NCC_6H_4CN, 83.0%).

$[p\text{-}C_6H_4(\overline{CNSNS})_2][SbCl_6]_2$. An excess of $SbCl_5$ (1 cm^{-3}) was added to a suspension of $[p\text{-}C_6H_4(\overline{CNSNS})_2]Cl_2$ (0.335 g, 1 mmol) in CH_2Cl_2 at room temperature. On agitation this soon yielded a fine pale cream precipitate of $[p\text{-}C_6H_4(\overline{CNSNS})_2][SbCl_6]_2$ which was filtered off and washed with CH_2Cl_2 to remove unreacted $SbCl_5$. Yield: 0.906 g, 95%. IR: ν_{max}/cm^{-1} 1503m, 1430s, 1390s, 1292m, 1242w, 1222w, 1207w, 1132m, 1013w, 970s, 897m, 881s, 836s, 788s, 720m, 658m, 625m, 580m and 550s.

$[p\text{-}C_6H_4(\overline{CNSNS})_2]Br_2$. The salt $[p\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$ (0.662 g, 1 mmol) and a slight molar excess of

Table 2 Atomic coordinates ($\times 10^4$) for $p\text{-}C_6H_4(\overline{CNSNS})_2$

Atom	*x*	*y*	*z*
S(1)	3 132(2)	13 136(2)	1 203(1)
N(1)	6 176(6)	12 373(6)	829(5)
S(2)	7 458(2)	9 743(2)	1 702(1)
C(1)	4 746(7)	9 285(7)	2 845(5)
N(2)	2 754(6)	10 933(6)	2 591(5)
C(2)	4 875(7)	7 087(6)	3 962(5)
C(3)	2 768(6)	6 741(6)	4 926(5)
C(4)	7 132(6)	5 259(8)	4 055(5)

Table 3 Bond lengths (Å) and angles (°) for $p\text{-}C_6H_4(\overline{CNSNS})_2$

S(1)–N(1)	1.659(4)	S(1)–N(2)	1.646(4)
N(1)–S(2)	1.632(4)	S(2)–C(1)	1.775(4)
C(1)–N(2)	1.276(4)	C(1)–C(2)	1.476(5)
C(2)–C(3)	1.397(5)	C(2)–C(4)	1.424(5)
C(3)–C(4′)	1.346(6)		
N(1)–S(1)–N(2)	102.2(2)	S(1)–N(1)–S(2)	110.8(2)
N(1)–S(2)–C(1)	97.0(2)	S(2)–C(1)–N(2)	115.7(3)
S(2)–C(1)–C(2)	120.2(3)	N(2)–C(1)–C(2)	124.1(4)
S(1)–N(2)–C(1)	113.7(3)	C(1)–C(2)–C(3)	120.6(3)
C(1)–C(2)–C(4)	120.9(3)	C(3)–C(2)–C(4)	118.5(3)
C(2)–C(3)–C(4′)	121.0(3)	C(2)–C(4)–C(3′)	120.5(3)

[NEt$_4$]Br (0.60 g, 2 mmol) were stirred in CH$_3$CN to produce an instant crimson precipitae of $[p\text{-}C_6H_4(\overline{CNSNS})_2]Br_2$. The product was filtered off and then extracted with CH$_2$Cl$_2$ in a sealed extractor.[20] Yield: 0.400 g, 90%. IR: ν_{max}/cm^{-1} 1505w, 1427m, 1396m, 1290m, 1245w, 1222w, 1150m, 1005w, 964s, 910m, 855m, 838s, 767s, 720m, 697s, 660m, 628m, 580s and 552s.

This salt was also prepared by condensation of excess liquid bromine onto a frozen solution of $p\text{-}C_6H_4(\overline{CNSNS})_2$ in CH$_2$Cl$_2$. On allowing to warm to room temperature the black precipitate was replaced by a deep burgundy-red precipitate of $[p\text{-}C_6H_4(\overline{CNSNS})_2]Br_2$. The material was isolated by pumping to dryness and had the same analysis and IR spectrum as above.

$[p\text{-}C_6H_4(\overline{CNSNS})_2][S_3N_3]_2$.—The salt $[p\text{-}C_6H_4(\overline{CNSNS})_2][AsF_6]_2$ (0.662 g, 1 mmol) and a slight molar excess of [NPr$_4$][S$_3$N$_3$] (0.648 g, 2 mmol) were stirred in CH$_2$Cl$_2$ to produce an instant black-green precipitate of $[p\text{-}C_6H_4(\overline{CNSNS})_2][S_3N_3]_2$. The product was filtered off and then extracted with CH$_2$Cl$_2$ in a sealed extractor.[20] Yield: 0.448 g, 80%. IR: ν_{max}/cm^{-1} 1510w, 1400s, 1310w, 1235m, 1120m, 1015w, 892m, 852w, 838s, 730s, 692s, 665s, 640s, 600s and 566m.

$p\text{-}C_6H_4(\overline{CNSNS})_2$. The salt $[p\text{-}C_6H_4(\overline{CNSNS})_2]Cl_2$ (0.355 g, 1 mmol) and a slight molar excess of SbPh$_3$ (0.355 g, 1 mmol) were stirred in CH$_2$Cl$_2$ to produce a blue-black precipitate of $p\text{-}C_6H_4(\overline{CNSNS})_2$ over a period of 1 h. The product was filtered off and then washed with CH$_2$Cl$_2$ (5 × 5 cm^3). Yield: 0.256 g, 90%. IR: ν_{max}/cm^{-1} 1405m, 1380m, 1225m br, 1110mw,br, 1010s, 925s, 827s, 792m, 775m, 703s, 655w, 640m, 595s, 560w, 540m, 465w br, 400w, 325m and 310s.

Larger polycrystalline masses were formed over a period of 72 h by slow diffusion of SbPh$_3$ in CH$_2$Cl$_2$, through a grade 3 glass sinter, into a concentrated CH$_2$Cl$_2$ solution of $[p\text{-}C_6H_4(\overline{CNSNS})_2]Cl_2$ over excess $[p\text{-}C_6H_4(\overline{CNSNS})_2]Cl_2$. From these samples suitable needles for X-ray study were cut in the open air and mounted in glass Lindemann capillaries.

Crystal-structure Determination.—*Crystal data.* C$_8$H$_4$N$_4$S$_4$, $M = 284.4$, triclinic, $P\bar{1}$, $a = 5.772(1)$, $b = 6.382(1)$, $c = 7.491(1)$ Å, $\alpha = 79.21(1)$, $\beta = 82.86(1)$, $\gamma = 70.25(1)°$, $U = 254.6$ Å^3 (from 2θ values between 30 and 60° of 32 reflections measured at $\pm\omega$), $Z = 1$, $D_c = 1.855$ g cm^{-3}, $F(000) = 144$, λ(Cu-Kα) = 1.541 84 Å, $\mu = 8.27$ mm^{-1}, $T = 298$ K.

Data collection and processing. A crystal of size 0.24 × 0.28 mm and thickness <0.01 mm, sealed in a Lindemann glass capillary, was examined on a Stoe–Siemens diffractometer. A complete sphere of data was collected by ω–θ scans and an on-line profile-fitting method;[21] $2\theta_{max} = 130°$ and maximum indices were h 6, k 7, l 8. A correction was made for a *ca.* 3% intensity decay in standard reflections, together with semi-empirical absorption corrections,[22] giving transmission factors in the range 0.15–1.00. From 1554 measured reflections, 793 unique data were obtained, and 678 with $F > 4\sigma_c(F)$ were used for structure determination; $\sigma_c(F)$ values were based on counting statistics only. $R_{int} = 0.025$ for the merging of equivalent reflections.

Structure solution and refinement. All C, N and S atoms of the crystallographically unique half molecule were located by direct methods, and H atoms were added in calculated positions on the ring angle external bisectors, with C–H 0.96 Å and $U(\text{H}) = 1.2U_{eq}(\text{C})$. Refinement minimised $\Sigma w(|F_o| - |F_c|)^2$, with $w^{-1} = \sigma^2(F) = \sigma_c{}^2(F) + 5 - 12G + 43G^2 - 14H + 10H^2 + 16GH$ ($G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$),[23] and anisotropic thermal parameters were refined for all non-hydrogen atoms. Extinction effects were negligible. Atomic scattering factors were taken from ref. 24. At convergence, $R = 0.077$, $R' = (\Sigma w\Delta^2/\Sigma wF_o{}^2)^{\frac{1}{2}} = 0.067$, goodness of fit = 1.36 for 74 parameters; the largest shift/e.s.d. was 0.005 and the largest peak in a final difference synthesis was 0.69 e Å^{-3}.

Refined atomic coordinates are given in Table 2, bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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References

1 A. Vegas, A. Pérez-Salazar, A. J. Banister and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1980, 1812.

2 A. J. Banister, I. B. Gorrell, W. Clegg and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1989, 2229.

3 A. J. Banister, I. B. Gorrell, W. Clegg and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1991, 1105.

4 R. Mews, *Chem. Ber.*, 1985, **118**, 3781.

5 A. J. Banister, M. I. Hansford, Z. V. Hauptman, A. W. Luke, S. T. Wait, W. Clegg and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1990, 2793.

6 L. Alcaer (editor), *The Physics and Chemistry of Low Dimensional Solids*, R. Deidel, Dordrecht, 1980.

7 R. G. Hey, Ph.D. Thesis, University of Durham, 1980.

8 G. K. MacLean, J. Passmore, M. N. S. Rao, M. J. Schriver and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1985, 1405.

9 W. V. F. Brooks, N. Burford, J. Passmore, M. J. Schriver and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 69.

10 N. Burford, J. Passmore and M. J. Schriver, *J. Chem. Soc., Chem. Commun.*, 1986, 140.

11 A. J. Banister and A. G. Kendrick, *J. Chem. Soc., Dalton Trans.*, 1987, 1565.

12 A. J. Banister, R. G. Hey, G. K. MacLean and J. Passmore, *Inorg. Chem.*, 1982, **21**, 1679.

13 A. J. Banister, A. W. Luke and J. M. Rawson, unpublished work.

14 S. C. Nyburg and C. H. Faerman, *Acta Crystallogr., Sect. B*, 1985, **41**, 274.

15 G. P. Charbonneau and Y. Delugeard, *Acta Crystallogr., Sect. B*, 1977, **33**, 1586.

16 P. D. B. Belluz, A. W. Cordes, E. M. Kristof, P. V. Kristof, S. W. Liblong and R. T. Oakley, *J. Am. Chem. Soc.*, 1989, **111**, 9276.

17 A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, in the press.

18 J. Bojes and T. Chivers, *Inorg. Chem.*, 1978, **17**, 318.

19 S. T. Wait, Ph.D. Thesis, University of Durham, 1989.

20 R. W. H. Small, A. J. Banister and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1984, 1377.

21 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

22 G. M. Sheldrick, SHELXTL, an integrated system for solving, refining and displaying crystal structures from diffraction data, Revision 5, University of Göttingen, 1985.

23 Wang Hong and B. E. Robertson, *Structure and Statistics in Crystallography*, ed. A. J. C. Wilson, Academic Press, New York, 1985, p. 125.

24 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

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