The Preparation of some 4-Phenyl-1,2,3,5-dithiadiazolium Salts and a Dimeric 4-Phenyl-1,2,3,5-dithiazole, (PhCN₂S₂)₂

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4-Phenyl-1,2,3,5-dithiadiazolium chloride, $(PhCN_2S_2)Cl$, has been converted into further salts, $(PhCN_2S_2)X$, where X = $FeCl_4$, Br, and NCS. Syntheses of $(CH_3CN_2S_2)Cl$ and $(p\text{-}ClC_6H_4CN_2S_2)Cl$ are also described. $(PhCN_2S_2)Cl$ is reduced by metals (*e.g.* Zn/Cu) to give $(PhCN_2S_2)_2$ which is isoelectronic with $S_6N_4{}^{2+}$.

Most cyclic thiazenes, containing two co-ordinate sulphur, are planar (or close to planar) Hückel species (*e.g.* 10π $S_4N_3{}^+$ and 14π $S_5N_5{}^+$).[1] There is one major exception, the cation in $S_6N_4(ClS_2O_6)_2$ and $S_6N_4(AsF_6)_2$; these salts do not contain a planar 14π monocyclic $S_6N_4{}^{2+}$. *X*-Ray studies[2] of S_6N_4-$(ClS_2O_6)_2$ reveal $S_3N_2{}^+$ cations associated in a unique type of ' stepped dimer' arrangement. The cation in the hexafluoro-arsenate is similarly associated (Figure 1a) and shows a five line e.s.r. spectrum in which the unpaired electron in the $S_3N_2{}^+$ ring is coupled to the two equivalent nitrogen atoms.[3] The dithiadiazolium cation (1) is an isoelectronic analogue of $S_3N_2{}^{2+}$ (2). Several salts of (1) have been prepared[4-6] and further derivatives are described in this paper. Dithiadiazolium salts (1; R = Ph) can be reduced to $(PhCN_2S_2)_2$. The monomer is a neutral analogue of $S_3N_2{}^+$ and both show an e.s.r. spectrum characteristic of a single unpaired electron.

(1)   (2)

Figure 1. Crystal structures of (a) $S_6N_4(AsF_6)_2$ after Gillespie[18] and (b) $(PhCN_2S_2)_2$ after Vegas[15]

Experimental

I.r. spectra (250—4 000 cm⁻¹) of Nujol mulls prepared under nitrogen, were recorded using KBr plates and a Perkin-Elmer 577 prism grating spectrophotometer. Mass spectra were obtained on an AEI MS9 mass spectrometer at 70 eV with an accelerating potential of 8 keV. Solvents and liquid reagents were purified as follows: toluene, pentane, and diethyl ether were stored over sodium wire. Nitromethane and carbon tetrachloride were dried over P_4O_{10}, distilled twice and stored over activated molecular sieve (3A). Acetonitrile, benzo-nitrile, and nitrobenzene were dried over $MgSO_4$ and fraction-ally distilled. Acetonitrile was stored over activated molecular sieve (3A). Sulphur dichloride, sulphuryl chloride, and thionyl chloride were purified by fractional distillation. Tetrahydro-furan (THF) was refluxed over sodium–potassium alloy and fractionally distilled. Chlorine gas was dried by passing through a tower of P_4O_{10}. Ammonium chloride, potassium bromide, and ammonium thiocyanate were dried in an oven at 120 °C. Other reagents were AnalaR grade used without further purification. $S_3N_2Cl_2$ was characterised by its i.r. spectrum (Nujol mull) with absorptions at 1 015m, 940s, 710s, 578m, 459ms, 403s, and 380ms cm⁻¹.

4-Phenyl-1,2,3,5-dithiadiazolium Chloride.—(i) *From* NH_4Cl, SCl_2, *and* PhCN. This is an improved version of an earlier preparation.[5] A suspension of ammonium chloride (20 g, 0.37 mol) in sulphur dichloride (100 ml, 1.58 mol) and benzo-nitrile (38 ml, 0.37 mol) was refluxed (10 h; 100—120 °C) in a two-necked flask (500 ml) fitted with a reflux condenser with a stream of dry chlorine passing at a rate of 60 mm² s⁻¹. (If the chlorine flow is stopped for longer than 15 min orange crystals of $S_3N_2Cl_2$ form in the condenser.) The mixture was cooled to 0 °C, filtered, and the crude product (33.2 g) was washed with ether (4 × 20 ml) and recrystallised (23.3 g, 30% based on benzonitrile) from liquid sulphur dioxide
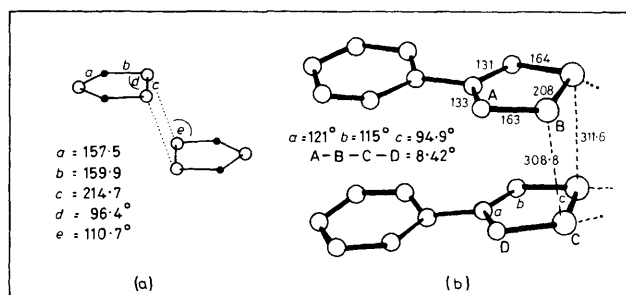
(15 g g⁻¹) (Found: C, 38.5; H, 2.7; Cl, 15.9; N, 12.2; S, 29.9. Calc. for $C_7H_5ClN_2S_2$: C, 38.8; H, 2.3; Cl, 16.4; N, 12.9; S, 29.6%); $v_{max.}$ 1 600w, 1 392m, 1 346w, 1 150m, 1 073m, 1 028m, 1 000w, 921m, 893s, 842s, 784s, 702s, 690m,sh, 549s, 515w, and 472w cm⁻¹.

(ii) *From* NH_4Cl, SCl_2, *and toluene*. A suspension of ammonium chloride (10.0 g, 0.19 mol) in sulphur dichloride (50 ml, 0.79 mol) and toluene (125 ml, 1.17 mol) was stirred (10 h, 140 °C) in a two-necked flask (500 ml) fitted with a water condenser. The mixture was filtered hot (grade one sinter). The filtrate was cooled to −20 °C, filtered, and the crude solid product recrystallised from nitrobenzene (1.1 g, 3% based on ammonium chloride), $v_{max.}$ 1 594m, 1 397m, 1 350m,sh, 1 148mbr, 1 065w, 1 025w, 1 000w, 920mw, 890vs, 842ms, 792m, 780m, 708mw, 694vs, and 542ms cm⁻¹.

(iii) *From 4-Phenyl*-1,2,3,5-*dithiadiazole dimer and sul-phuryl chloride.* $(PhCN_2S_2)_2$ (0.13 g, 0.36 mmol) was stirred for 1 h at room temperature with sulphuryl chloride (30 ml) and filtered to give a yellow solid which was washed with pentane (5 × 10 ml) to give the product [0.13 g, 83% based on $(PhCN_2S_2)_2$] (Found: C, 38.3; H, 1.6; Cl, 17.5; N, 12.7; S, 29.2%); $v_{max.}$ 1 594mw, 1 395ms, 1 150m, 1 065w, 1 028m, 1 000w, 920m, 890s, 842s, 781m, 698vs, and 544m cm⁻¹.

4-Phenyl-1,2,3,5-dithiadiazolium Tetrachloroferrate(III).—Iron(III) chloride (2.25 g, 13.9 mmol) was stirred for 6 h at room temperature with 4-phenyl-1,2,3,5-dithiadiazolium chloride (3.0 g, 13.9 mmol) in thionyl chloride (40 ml). The mixture was filtered and the crude product recrystallised from

thionyl chloride (20 ml g^{-1}) to give bright orange platelets (4.7 g, 89%) (Found: C, 22.0; H, 1.5; Cl, 37.0; N, 7.6; S, 16.9. Calc. for C$_7$H$_5$Cl$_4$N$_2$S$_2$Fe: C, 22.2; H, 1.3; Cl, 37.4; N, 7.4; S, 16.9%); $\nu_{max.}$ 1 608w, 1 600w, 1 588w, 1 507m, 1 409vs, 1 402vs, 1 347s, 1 300m, 1 201s, 1 169s, 1 100w, 1 035m, 998w, 935s, 920vs, 848m, 780vs, 729m, 702vs, 688s, 672m, 566s, 412s, 392s, 369s, and 340s cm^{-1}
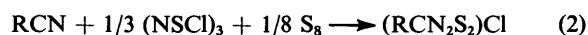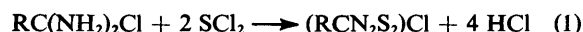
Table 1. Experimental conditions for the reduction of phenyl dithiadiazolium chlorides by metals

| Metal (excess)	Solvent	Conditions
Zn/Cu	THF	Room temp.

Table 2. Known dithiadiazolium salts categorised according to their colour

Salt [6–8]	Group A	Group B
$PhCN_2S_2Cl$	Orange	
$PhCN_2S_2Br$	Red	
$PhCN_2S_2BF_4$	Red	
$PhCN_2S_2BCl_4$	Orange	
$PhCN_2S_2SbCl_6$	Red	
$PhCN_2S_2PF_6$	Orange	
$(PhCN_2S_2)_2SnCl_6$	Yellow	
$PhCN_2S_2FeCl_4$	Orange	
$PhCN_2S_2NCS$		Purple-black
$PhCN_2S_2CH_3CO_2$		Purple-black
$PhCN_2S_2PhCO_2$		Purple-black

The ionic compounds (4) (*e.g.* X = Cl) with two adjacent sulphur atoms, are usually prepared from an amidinium salt and sulphur dichloride (equation 1) [5]; or by treating $(NSCl)_3$ with a nitrile (equation 2) [4,5] or an azine (equation 3).[6]

$$RC(NH_2)_2Cl + 2\ SCl_2 \longrightarrow (RCN_2S_2)Cl + 4\ HCl \quad (1)$$

$$RCN + 1/3\ (NSCl)_3 + 1/8\ S_8 \longrightarrow (RCN_2S_2)Cl \quad (2)$$

$$3\ RCH{=}N{-}N{=}CHR + 4\ (NSCl)_3 \longrightarrow$$
$$6\ (RCN_2S_2)Cl + 3\ N_2 + 6\ HCl \quad (3)$$

A fourth method involves treating a nitrile with sulphur dichloride and ammonium chloride (equation 4). An improved version of the published preparation [5] is described in the Experimental section above, in which the $S_3N_2Cl_2$ by-product is avoided by passing chlorine gas through the reaction mixture.

$$RCN + 2\ SCl_2 + NH_4Cl \longrightarrow (RCN_2S_2)Cl + 4\ HCl \quad (4)$$
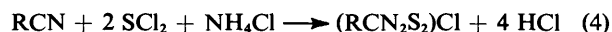
Both the reaction time and consumption of SCl_2 are reduced by this procedure and the yield of $PhCN_2S_2Cl$ is increased slightly (from 25% [5] to 30%). 4-Phenyl-1,2,3,5-dithiadiazolium chloride was also isolated from the reaction of toluene with SCl_2 and NH_4Cl. This is the first known example of dithiadiazolium ring synthesis from a hydrocarbon starting material.

Nitromethane, nitrobenzene, toluene, and liquid sulphur dioxide have all been used to purify $(PhCN_2S_2)Cl$. In the case of recrystallisation from toluene, high C and H analyses, combined with low N, S, and Cl, suggested the presence of toluene of recrystallisation [a ratio of $(PhCN_2S_2)Cl$: toluene of 6 : 1 according to X-ray analysis].[10] Purest samples of $(PhCN_2S_2)Cl$ were obtained after double recrystallisation from nitrobenzene.

Several compounds have been made containing the $PhCN_2$-$S_2{}^+$ cation with various stabilising anions $[SbCl_6{}^-, CF_3SO_6{}^-, (NSO_2F)_2{}^-, BF_4{}^-$ and $PF_6{}^-$ [6–8] and (in this paper) Br^-, NCS^-, and $FeCl_4{}^-$]. Tetrachloroborate and hexachlorostannate(IV) salts are also easily prepared by the action of the relevant Lewis acid on solutions of $(PhCN_2S_2)Cl$ in liquid sulphur dioxide and thionyl chloride, respectively. However, thiocyanate, benzoate, and acetate salts could only be isolated from metathetical reactions [involving $(PhCN_2S_2)Cl$ and NH_4NCS, $PhCO_2Na$, and CH_3CO_2Na, respectively] in liquid sulphur dioxide at room temperature. In organic solvents such as THF, these salts, believed to be formed as intermediates, were unstable and decomposed to give 4-phenyl-1,2,3,5-dithiadiazole $(PhCN_2S_2)_2$.

Known dithiadiazolium salts are either brightly coloured,

Table 3. A comparison of i.r. absorptions (cm^{-1}) in some dithiadiazolium salts

Cl^-	$FeCl_4{}^-$	Br^-	NCS^-
1 392	1 402, 1 409	1 452	1 449
1 150	1 169	1 152	1 148, 1 178
	1 035	1 025	1 023
921	935	922	923
893	920	897	900
842	848	840	843
784	780	782	780
702	702		690
690	688	695	679, 688
549	566	543	552

Table 4. I.r. frequencies (cm^{-1}) corresponding to fundamental ring vibrations in $RCN_2S_2{}^+$

$(CH_3CN_2S_2)Cl$	$(PhCN_2S_2)Cl$	$(Cl{\cdot}C_6H_4{\cdot}CN_2S_2)Cl$
861	890	890
848	842	846
535	543	540

yellow to red (Table 2, Group A) or are purple-black (Group B), the latter containing more polarisable anions. In these salts the anticipated, larger degree of cation–anion interaction facilitates the electron transfer, which occurs readily in organic solvents, with the formation of the neutral dimer (equation 5).

$$2\ PhCN_2S_2{\cdot}NCS \longrightarrow 2\ PhCN_2S_2 + 2\ NCS \longrightarrow$$
$$(PhCN_2S_2)_2 + (NCS)_2 \quad (5)$$
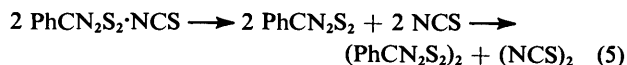
Although the general pattern and position of bands in the i.r. and mass spectra of Group A and B salts suggests that the compounds are structurally similar to $(PhCN_2S_2)Cl$ [10] (even in the Group B salts there is no serious perturbation of the vibrational spectrum of the cation), the i.r. data (Table 3) do provide some evidence of a trend towards cation–anion interaction in the series $Cl^- \longrightarrow FeCl_4{}^- \longrightarrow Br^- \longrightarrow NCS^-$. As the cation is increasingly perturbed (and the symmetry is lowered) there is an increase in the number of observed i.r. absorptions. No evidence was found for the presence of $(PhCN_2S_2)_2$ (characterised by strong absorptions at 1 139, 805, 655, and 511 cm^{-1}) in the Group B salts. Absorptions at 890, 842, and 543 cm^{-1} [in $(PhCN_2S_2)Cl$, Table 4] are probably fundamental vibrations of the dithiadiazolium ring, since they are the strongest bands in the spectra of $RCN_2S_2{}^+$ salts where R is aliphatic (*e.g.* CH_3).

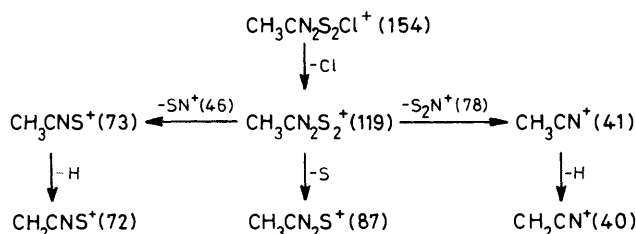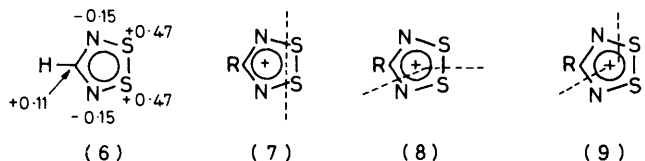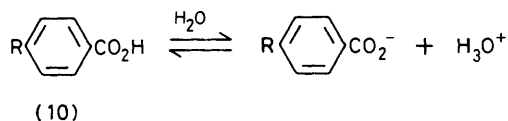*4-Methyl-1,2,3,5-dithiadiazolium Chloride.*—This compound has been previously prepared from acetonitrile, sulphur dichloride, and metal azides,[11] however the present method (Experimental section) is a more convenient medium-scale (5—10 g) preparation. The ^1H n.m.r. chemical shift obtained for $CH_3CN_2S_2Cl$ was compared with several standards (Table 5). As expected the methyl protons in $CH_3CN_2S_2Cl$ are more strongly deshielded than those in methylcyclohexane. The substituent groups $-CN$, $-CO_2H$ and $-NO_2$, however, are much more strongly deshielding than $-CN_2S_2{}^+$. An MNDO calculation [12] of the net atomic charges in $HCN_2S_2{}^+$ (6) has shown that most of the positive ring charge resides on the sulphur atoms. This is consistent with the small chemical shift observed for the protons in $CH_3CN_2S_2Cl$.

All the major mass spectral peaks were assigned and the fragmentation pattern (Scheme 1) is suggested. Three modes

Table 5. ^{1}H N.m.r. chemical shifts for some methyl compounds

Compound	δ_{CH_3} (p.p.m.) [a]
$CH_3(CH_2)_5CHO$	0.89
$CH_3CH(CH_2)_4CH_2$	0.92
$CH_3CN_2S_2Cl$	1.05
$(CH_3CH_2)_2O$	1.16
CH_3CN	1.95
CH_3CO_2H	2.05
CH_3NO_2	4.33

[a] R. M. Silverstein and G. C. Bassler, ' Spectrometric Identification of Organic Compounds,' 2nd edn, Wiley, N.Y., 1967, 135.

Table 6. Some values of the *para*-substituent constant, σ_p

Substituent	σ_p
$^-$OMe	-0.27 [13]
$^-$H	0.00 [13]
$^-CH_2CN$	0.01 [13]
$^-CH_2Cl$	0.18 [13]
$^-$Cl	0.23 [13]
$^-$CN	0.66 [a]
$^-NO_2$	0.78 [13]

[a] D. H. MacDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

Scheme 2.

Scheme 1.

of fragmentation have been observed for the $RCN_2S_2^+$ ring (7)—(9); however, the major route (based on spectral intensities) is usually *via* loss of S_2N^+ (9).
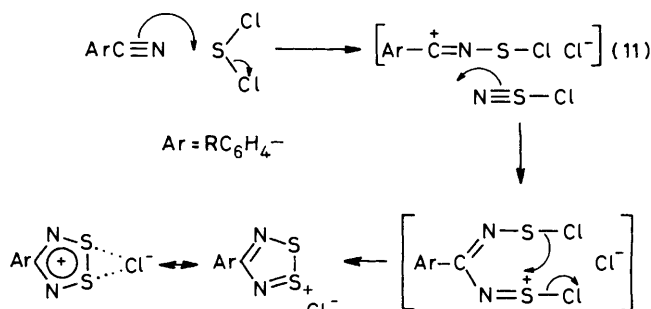
4-(4-Chlorophenyl)-1,2,3,5-dithiadiazolium Chloride.—Some consequences of the electron-withdrawing effect of the *p*-chlorine were observed for $(ClC_6H_4\cdot CN_2S_2)Cl$. Compared with $(PhCN_2S_2)Cl$ there is likely to be a stronger three centre interaction between the sulphurs and chlorine (*i.e.* increased cation–anion interaction) and greater susceptibility of the ring to nucleophilic attack [which rationalises the observed increase in moisture sensitivity compared with $(PhCN_2S_2)Cl$]. Attempted syntheses of the compounds $(RC_6H_4\cdot CN_2S_2)Cl$ where $R = Cl$, CN, and NO_2 (electron-withdrawing groups chosen to gain insight into the mechanism of nitrile reaction with SCl_2 and NH_4Cl) produced only the *p*-chloro derivative. A measure of side-group conjugation with benzene, and of nitrile nucleophilicity, was gained by inspection of σ_p values. σ_p, the *para*-substituent constant, is defined as $\log(K_p/K_o)$ where K_p and K_o are equilibrium constants for hydrolysis of, respectively, substituted (10) and unsubstituted benzoic acids. At 25 °C, $K_o = 6.26 \times 10^{-5}$.[13] Presumably since the *p*-cyano and *p*-nitro groups are more strongly electronegative than *p*-chloro (Table 6), nitrile nucleophilicity in $R\cdot C_6H_4\cdot CN$ (for $R = CN$, NO_2, compared with $R = H$) is reduced to the

extent where reaction with SCl_2 and NH_4Cl (as in Scheme 2) does not occur.

A suggested reaction mechanism for the nitrile reaction is shown in Scheme 2. Heal and Kane [14] have shown that strong Lewis bases readily displace chloride ion from sulphur dichloride and they suggested that the weak conductivity detected in the CH_3CN/SCl_2 system was due to the presence of a low concentration of $(CH_3CNSCl)^+$ (11).

4-Phenyl-1,2,3,5-dithiadiazole.—This is formed by the reduction of $PhCN_2S_2^+$ (conveniently as the chloride salt). Effective reducing agents (in organic solvents, generally at room temperature) include sodium thiocyanate, lithium azide, potassium cyanide, phenylmagnesium bromide, n-butyl-lithium and tin(II) chloride. The reaction involving sodium thiocyanate was described in an earlier paper.[15] The neutral dimer can also be prepared, as mentioned above, by thermal decomposition of $(PhCN_2S_2)X$ where $X =$ thiocyanate, benzoate, or acetate; however, the best preparations (Experimental section) involve reduction by metals (equation 6), especially zinc, with further purification by sublimation.

$$x\ PhCN_2S_2Cl + M \xrightarrow{\text{THF}} x/2\ (PhCN_2S_2)_2 + MCl_x \quad (6)$$
$$M = Zn\ \text{or}\ Hg$$
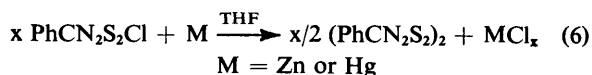
$(PhCN_2S_2)_2$ is rapidly hydrolysed by atmospheric moisture, and thus it is recommended that the compound be stored as relatively large crystals, grown by careful recrystallisation from THF, monoglyme, or 1,2-dichloroethane.

4-Phenyl-1,2,3,5-dithiadiazolium iodide (prepared from $PhCN_2S_2Cl$ in a method similar to that described for $PhCN_2$-S_2Br above) was found to disproportionate in liquid sulphur dioxide at room temperature, to give the neutral dimer and iodine (equation 7). It is probable, therefore, that $PhCN_2S_2I$ is a Group B type salt in which there is strong cation–anion interaction.

$$2\ PhCN_2S_2Cl + 2\ KI \xrightarrow{SO_2} 2\ PhCN_2S_2I \rightleftharpoons$$
$$(PhCN_2S_2)_2 + I_2 \quad (7)$$
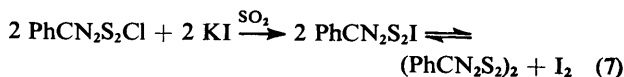
Table 7. A comparison of the I(3d) binding energy of $PhCN_2S_2I$ with other iodine compounds [a]

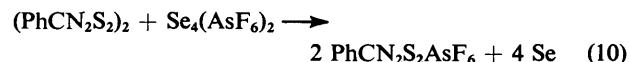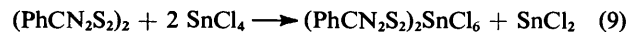| Compound	Binding energy I(3d)/eV
PhI	622.1
$PhCN_2S_2I$	620.7
$[Ph_2I^+]I^-$	619.7
KI	618.6

[a] R. G. Hey, unpublished results. For KI value see W. E. Morgan, J. R. Van Wazer, and W. J. Stec, *J. Am. Chem. Soc.*, 1973, **95**, 751.

Some evidence for this was obtained by determining the I(3d) binding energy for the salt (Table 7). Although the iodine in $PhCN_2S_2I$ is essentially ionic, the significant interaction with the cation increases the binding energy relative to that observed for a non-interacting iodide such as KI.

$(PhCN_2S_2)_2$ reacts rapidly with halogens *viz.* I_2, Br_2, Cl_2 [and the chlorine sources, $SOCl_2$, SO_2Cl_2, or $(NSCl)_3$] to give the corresponding dithiadiazolium halide. In the presence of an excess of iodine, $PhCN_2S_2I$ is stabilised as the tri-iodide (equation 8).

$$(PhCN_2S_2)_2 + I_2 \rightleftharpoons 2\ PhCN_2S_2I \xrightarrow{2\,I_2} 2\ PhCN_2S_2I_3 \quad (8)$$

The dimer also formed dithiadiazolium salts with oxidising Lewis acids, such as tin(IV) chloride (equation 9) and group 6 polycations (*e.g.* equation 10)[16] but did not react with unsaturated systems such as phenylacetylene or tetrasulphur tetranitride.

$$(PhCN_2S_2)_2 + 2\ SnCl_4 \longrightarrow (PhCN_2S_2)_2SnCl_6 + SnCl_2 \quad (9)$$

$$(PhCN_2S_2)_2 + Se_4(AsF_6)_2 \longrightarrow$$
$$2\ PhCN_2S_2AsF_6 + 4\ Se \quad (10)$$

Although there has been some confusion in the literature regarding the formulation of the thiodithiazyl cation (as $S_3N_2^+$ or $S_6N_4^{2+}$), it is now generally accepted that the salts $S_2O_6Cl^-$,[2] $CF_3SO_3^-$,[17] and AsF_6^- [made by the oxidation of S_4N_4 with $S_8(AsF_6)_2$][18] contain the dimeric cation, $S_6N_4^{2+}$. The formulations $(S_3N_2)AsF_6$ and $(S_3N_2)CF_3SO_3$ had previously been suggested because solutions of these salts showed five-line e.s.r. spectra.[3,19] It now appears that the dimeric compounds dissociate to the monomer in solution. Monomeric $S_3N_2^+$ has been stabilised as solid $(S_3N_2)AsF_6$.[18]

Solid S_3N_2Cl has also been found to contain the $S_6N_4^{2+}$ cation[20] and, although, as expected, it does not show an e.s.r. spectrum at room temperature, a suspension of S_3N_2Cl in SO_2–$SOCl_2$ (80 : 20, v/v) gives a clear (but rather complex) spectrum at $-180\ ^{\circ}C$ which is thought to be due to $S_3N_2^+$.[21]

In the solid-state e.s.r. spectrum of $(PhCN_2S_2)_2$ (Figure 2) the bandwidth (25 gauss) is broad compared with the diphenylpicrylhydrazyl (DPPH) standard. The spectroscopic splitting factor (g) was calculated to be *ca.* 2.00 which is characteristic of a single unpaired electron. It is possible therefore that dissociation to the monomer, similar to that observed in $S_6N_4^{2+}$ salts, exists in $(PhCN_2S_2)_2$ in the solid state.

$(PhCN_2S_2)_2$ and $S_6N_4^{2+}$ are structurally very similar; they can be regarded as containing two 6π units ($PhCN_2S_2^+$ and $S_3N_2^{2+}$ respectively) linked by two long S–S bonds (Figure 1) involved in a four-centre electron-pair interaction. Alternative models[18,22] treat the bonding between the S_3N_2 rings in $S_6N_4^{2+}$ as a four-centre six-electron interaction; this effectively views the molecule as two four-electron (sulphur
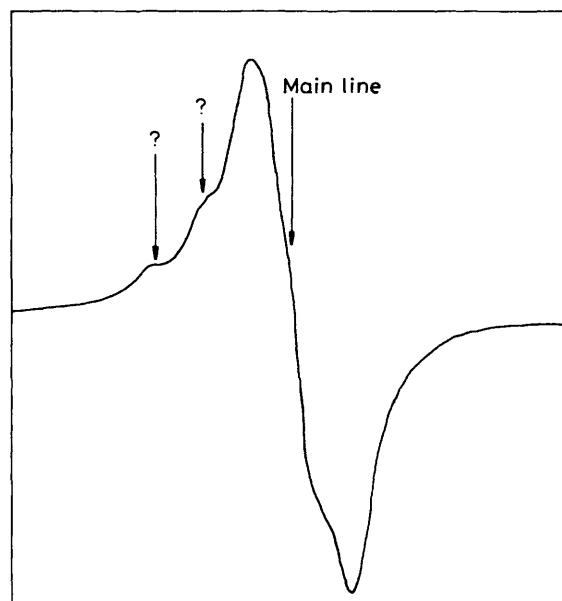

Figure 2. E.s.r. spectrum (derivative plot) of $(PhCN_2S_2)_2$, line width = 25 gauss (broad compared with the DPPH standard)

di-imide) ligands co-ordinated to an S_4^{2+} (6π) unit. However, S–N bond lengths in the S_3N_2 ring differ by a maximum of only 0.06 Å (*cf.* a difference of 0.05 Å in S–N bonds in $S_4N_3^+$[10] which is generally regarded as a 10π delocalised system).[23] Gillespie[18] reported that, based on bond lengths, ' all the S–N bonds in the $S_3N_2^+$ ring must have some double-bond character '. In addition, both the ring plane and external $\stackrel{\frown}{NSS}$ bond-angles (96.4 and 110.7°, respectively, Figure 1) would more closely fit sp^3-hybridisation at sulphur (discussed by Gillespie) than the sp^2-hybridisation used in the MO model described by Gleiter.[22] Perhaps the bonding in $S_6N_4^{2+}$ can be more adequately described by considering a σ-framework of sp^2-hybridised sulphur and nitrogen atoms in the N–S–N section of each ring, with sp^3-hybridisation at the disulphide sulphurs. Five π-MO's result from combination of the remaining p_π and sp^3 hybrid orbitals (with each sulphur atom contributing two, and each nitrogen one electron to the π-system). Since the HOMO of each $S_3N_2^+$ ring is singly occupied, these can be combined to give bonding and antibonding interactions (Figure 3). The slightly longer disulphide sulphur to nitrogen bonds are then a consequence of the reduced p_π–sp^3 hybrid orbital overlap.

A similar four-centre electron-pair MO description can be developed for $(PhCN_2S_2)_2$. Solid-state intermolecular interactions in the dithiadiazole dimer (*e.g.* S $\cdots$ N distances, 3.09—3.17 Å, are similar to the S $\cdots$ S intramolecular interaction)[15] are probably important in stabilising a *cis* rather than a *trans* structure.

In summary, a large number of 1,2,3,5-dithiadiazolium compounds can be synthesised with a variety of 4-substituents and stabilising anions. The reduced form of the 4-phenyl compound, $(PhCN_2S_2)_2$, has been prepared. The short intermolecular distances in $(PhCN_2S_2)_2$ all involve sulphur; thus, presumably the *cis* arrangement is adopted to achieve most compact crystal packing and the best exposure of sulphur atoms for secondary interactions. Other interatomic distances give no suggestion of interactions involving the phenyl substituent, thus stability is unlikely to be affected by bending due to bulky 4-substituents. The preparation of a variety of dithiadiazole dimers should therefore be possible.
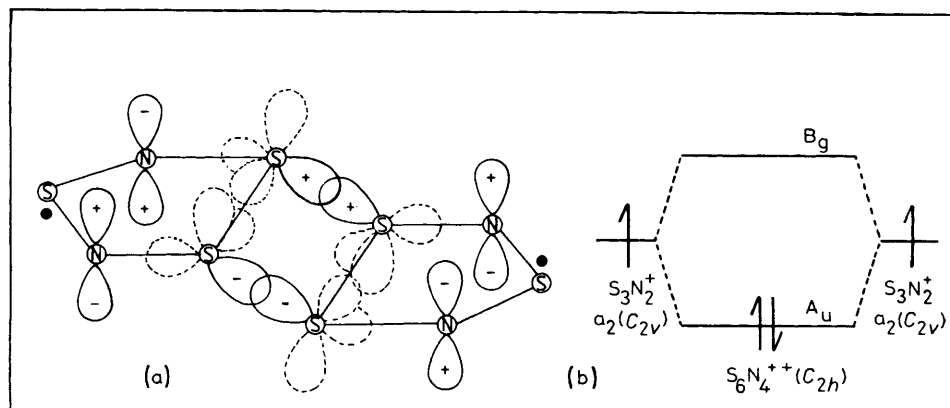
Figure 3. (a) and (b) Qualitative MO description of the four-centre electron-pair interaction in $S_6N_4{}^{2+}$. The HOMO of each S_3N_2 ring has a_2 symmetry (C_{2v} point group)

To date, attempted preparations of $(Bu^tCN_2S_2)_2$ and $(Cl_3C-CN_2S_2)_2$ have been unsuccessful. A crystal study is in progress on $(CH_3CN_2S_2)_2$.[24]

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