Direct Insertion of a Nitrogen Atom into the S–S Bond of a 1,2,3,5-Dithiadiazole Ring in a Direct Current Nitrogen Glow Discharge, and *X*-Ray Crystal Structure of 4-Methyl-1,2,3,5-dithiadiazole†

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Dimeric aryldithiadiazoles $(RCNSSN)_2$ (R = Ph or p-ClC_6H_4,) were treated with atomic nitrogen, generated in a cool direct current plasma, to form the corresponding dithiatriazine dimers by nitrogen insertion into the S–S bonds; alkyl derivatives (R = Me, Pr, or Bu^t) gave polymeric products. Dithiadiazolylium salts $[RCNSSN]^+X^-$ (R = Ph or p-ClC_6H_4; X = I, Br, CN, or S_3N_3) also reacted with nitrogen plasma to give high yields of the respective dithiatriazine $(RCN_3S_2)_2$. Structural criteria for the reaction are discussed. The crystalline methyldithiadiazole contains planar CNSSN rings with S–S 2.076(2), S–N 1.636(3), C–N 1.324(5) Å, N–S–S 94.5(1), C–N–S 114.5(3), and N–C–N 122.2(4)° (all average values). Within the dimer unit the parallel monomer rings are linked *via* one weak S ••• S bond (3.10 Å). The crystals are triclinic, space group $P\bar{1}$, with a = 11.296(1), b = 12.498(1), c = 14.647(2) Å, α = 72.06(1), β = 77.85(1), γ = 77.30(1)°, and Z = 8.

Numerous organothiazyl compounds, with organic groups incorporated into an $(SN)_x$ chain, have been prepared[1] in, as yet unsuccessful, attempts to obtain highly conductive analogues of $(SN)_x$ (for which σ = 1 000—3 000 S cm^{-1}).[2]

During our examination[3] of dithiadiazoles and dithiadiazolium salts as possible precursors to conductive C/S/N polymers, we noticed that when a sample of $(MeCNSSN)_2$, sealed under nitrogen, was subjected to a Tesla discharge, a non-conducting brown C/S/N polymer formed rapidly on the surface of the purple-black crystals. To assess the synthetic potential of this technique [but using a less energetic, and hence less destructive, direct current (d.c.) plasma] we exposed, to a d.c. nitrogen plasma, a variety of low volatility 1,2,3,5-dithiadiazoles and their respective dithiadiazolium salts, *e.g.* bromides and iodides (the anions were chosen to facilitate *in situ* formation of dithiatriazine with release of halogen). High (chemical) yield (75—80%) conversions into $(RCN_3S_2)_2$ (R = aryl) were obtained.

There are very few other examples of nitrogen fixation by sulphur compounds at ambient temperatures. Smith and Jolly[4] reported that atomic nitrogen (from a microwave discharge) reacted with S_2Cl_2 vapour to give $(NSCl)_3$. This compound is, however, more conveniently prepared by refluxing S_2Cl_2 over NH_4Cl.[5] The plasma method has also been used[6] to convert NH_3–H_2S and N_2–H_2S mixtures into impure amorphous $(SN)_x$.

Experimental

Tetrasulphur tetranitride was prepared from sulphur dichloride and ammonia, and after washing with water was purified by extraction with dioxane and recrystallisation from benzene.[7]

The dithiadiazole dimer $(PhCN_2S_2)_2$ (**1**) was prepared by Zn–Cu couple reduction of $[PhCN_2S_2]^+Cl^-$ in liquid SO_2,[8] followed by sublimation. Needles as well as powder can be used for the plasma conversion into $(PhCN_3S_2)_2$ (**2**). The p-chlorophenyl derivative was prepared in an analogous manner from $[p$-$ClC_6H_4CN_2S_2]^+Cl^-$.

Purified nitrogen for the plasma discharge was bled from the line nitrogen, deoxygenated by passing over copper turnings at 300 °C, and dried by passing through two P_4O_{10} columns and a cold trap at −196 °C.

All reactions and solutions were handled in standard Schlenk apparatus under an atmosphere of dry nitrogen. Manipulation of air- and moisture-sensitive solids was carried out in an Vacuum/Atmospheres Corporation dry-box fitted with an HE493 Dri-Train. Thionyl chloride was purified by fractional distillation from triphenyl phosphite.[9] Sulphuryl chloride was also purified by fractional distillation.

Liquid SO_2 was dried prior to use, by standing over P_4O_{10} for 1 week and then distilling onto calcium hydride for storage. Toluene was stored for 18 h over $CaCl_2$, refluxed over P_4O_{10}, and then distilled and stored over sodium wire. Dichloromethane was refluxed over P_4O_{10}, followed by CaH_2, and then distilled and stored over molecular sieve (grade 4A, BDH Ltd.). All distillations, except of SO_2, were carried out under an atmosphere of dry nitrogen.

Infrared spectra were recorded as Nujol mulls between either KBr or CsI plates on a Perkin-Elmer 577 spectrometer. Mass spectra were recorded on a VG Analytical 7070E spectrometer using electron-impact (e.i.) and chemical ionisation (c.i.) modes. N.m.r. spectra were recorded on a Brüker AG250 spectrometer. Differential scanning calorimetry (d.s.c.) was carried out with a Mettler FP85 thermal analysis cell coupled to a Mettler FP80 central processor. Samples were cold-sealed in aluminium capsules.

The low-temperature bath, for plasma reactions involving the alkyl derivatives, was regulated using a Haake F3 bath circulator with methylated spirit as coolant. Sulphur was determined as $BaSO_4$ following oxygen combustion. Carbon, hydrogen, and nitrogen were determined by micro combustion in a Carlo Erba 1106 elemental analyser.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: Torr ≈ 133 Pa, eV ≈ 1.60×10^{-19} J, kWh = 3.6×10^6 J.

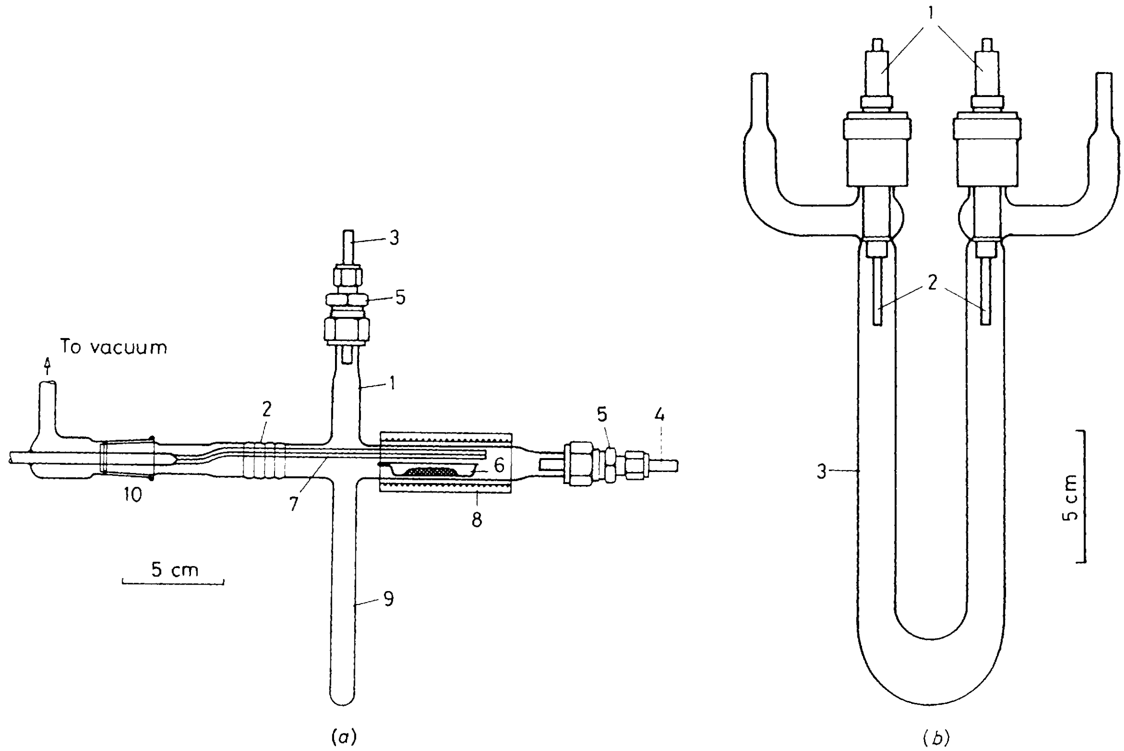


Figure 1. (*a*) Apparatus for the reaction of solids with a d.c. nitrogen plasma: 1 = quartz discharge tube; 2 = Pyrex to quartz graded joint; 3 and 4 = anode and cathode, both solid tungsten rods, diameter 6.35 mm; 5 = demountable vacuum feedthrough (adapted Swagelok $\frac{1}{2}$ to $\frac{1}{4}$ in reducing union; 6 = quartz boat; 7 = *ca.* 1 mm bore capillary; 8 = transparent resistance heater; 9 = volatiles trap; 10 = Young's greaseless joint. (*b*) Apparatus for the reaction of liquids and solids below room temperature with a d.c. nitrogen plasma: 1 = high-tension feedthrough (adapted Young's Teflon stemmed greaseless tap); 2 = solid tungsten rod, diameter 3.2 mm; 3 = Pyrex discharge tube with widened U bend

(1) *Plasma Conditions and the Preparation of* $(\mathrm{Ph\overline{CNSNSN}})_2$.—The compound $(\mathrm{Ph\overline{CNSSN}})_2$ (**1**) was transferred to the plasma tube [Figure 1(*a*)] in a glove-box. This tube was found suitable for exploratory work and small-scale synthesis, as high current densities could be maintained. Generally, a current of approximately 2 mA was used requiring 900 V—1 kV across the electrodes. The flow rate of dry nitrogen through the tube was maintained at approximately 70 Torr $\mathrm{cm^3\ s^{-1}}$ by balancing the bleed rate with the pumping speed. This gave an average residence time of approximately 2 s.

Compound (**1**) (0.25 g, 0.7 mmol), loosely heaped in a quartz boat, was immersed in the positive column of the discharge. Purified nitrogen was bled in *via* a needle valve through a capillary (internal diameter 0.5 mm) into the discharge tube [Figure 1 (*a*)]. The optimum reaction temperature (45 °C) was maintained throughout the reaction by an external heater (nichrome wire wound on a Pyrex tube). Under the above conditions the reaction was normally complete in about 10 h. The crude buff coloured product consisted of air-stable $(\mathrm{PhCN_3S_2})_2$ (**2**) and a small amount of black polymer. A very thin continuous polymeric film also formed on the walls of the discharge tube. Unreacted (**1**) was washed from the product with liquid $\mathrm{SO_2}$ using a closed extractor.[10] The pure product is largely insoluble in liquid $\mathrm{SO_2}$. A typical yield of (**2**) was 0.22 g (80%), and thus the energy consumption was 1.3×10^8 J $\mathrm{mol^{-1}}$ (*i.e.* 92 kW h $\mathrm{kg^{-1}}$) of the product (Found: C, 42.8; H, 2.1; N, 21.2; S, 32.9. $\mathrm{C_7H_5N_3S_2}$ requires C, 43.0; H, 2.6; N, 21.4; S, 32.8%; mass spectrum (c.i.), *m/z* 181 $(\mathrm{PhCNS_2})_2{}^+$ and 195 $(\mathrm{PhCN_3S_2})^+$, relative abundance 76 and 68% respectively]. Typical composition of the concomitant polymer was $\mathrm{C_3H_{2.5}NS}$; (Found: C, 41.4; H, 3.0; N, 18.0; S, 37.5%). D.s.c. (4 °C $\mathrm{min^{-1}}$); m.p. 118 °C (sharp endotherm), *cf.* lit.,[11] 115 °C, followed by immediate decomposition at 123 °C (sharp exotherm) leaving a purple melt. The i.r. spectra of (**1**) before and after nitrogenation are compared in Figure 2.

The unit-cell parameters of compound (**2**) given by Boeré *et al.*[11] were used to calculate the *X*-ray powder pattern.[12] This agreed very well with our observed pattern [(h,k,l) d_{hkl}/Å(obs.), d_{hkl}/Å(calc.)]: (001) 11.47, 11.51; (010) 10.22, 10.21; (011) 6.62, 6.60; ($\bar{1}$01) 5.82, 5.81; (021) 5.40, 5.40; (022) 4.70, 4.70.

(2) *Preparation of* $(p\text{-}\mathrm{ClC_6H_4\overline{CNSNSN}})_2$ (**4**) *from* $(p\text{-}\mathrm{ClC_6H_4\overline{CNSSN}})_2$ (**3**).—Compound (**3**) was prepared and purified as above for (**1**). The dark green powder (0.25 g, 1.15 mmol), again in a quartz boat, was immersed in the positive column of the discharge tube in the same way as in (1) above. The optimum reaction temperature was 60 °C and the reaction took about 12 h. The dark brown air-stable crude product (**4**) was purified as for (**1**) [Found: C, 36.7; H, 1.5; Cl, 15.1; N, 18.1; S, 27.4. $\mathrm{C_7H_4ClN_3S_2}$ requires C, 36.6; H, 1.7; Cl, 15.4; N, 18.3; S, 27.8%; mass spectrum (c.i.), *m/z* 230 $[p\text{-}\mathrm{ClC_6H_4CN_3S_2}]^+$, 29%, and 215 $[p\text{-}\mathrm{ClC_6H_4CN_2S_2}]^+$, 71%]. D.s.c. (4 °C $\mathrm{min^{-1}}$): 114.5 °C (endotherm) followed by decomposition at 118.2 °C. Infrared spectra of (3) and (**4**) are shown in Figure 2.

(3) *Preparation of* $(\mathrm{RCN_3S_2})_2$ *from* $[\mathrm{RCN_2S_2}]^+\mathrm{X}^-$ (R = Ph *or* $p\text{-}\mathrm{ClC_6H_4}$; X = CN, Br, *or* I).—Compounds $[\mathrm{RCN_2S_2}]^+\mathrm{X}^-$ (typically 1 mmol)[13] were placed in the positive column of the discharge under the same flow conditions and current densities as in (1). The temperature was maintained with a Eurotherm 821 controller. When $\mathrm{X = I^-}$ the reaction temperature was found to be 35 °C and reaction was complete in 8 h. A thick coating of polymer also formed on both the discharge tube walls

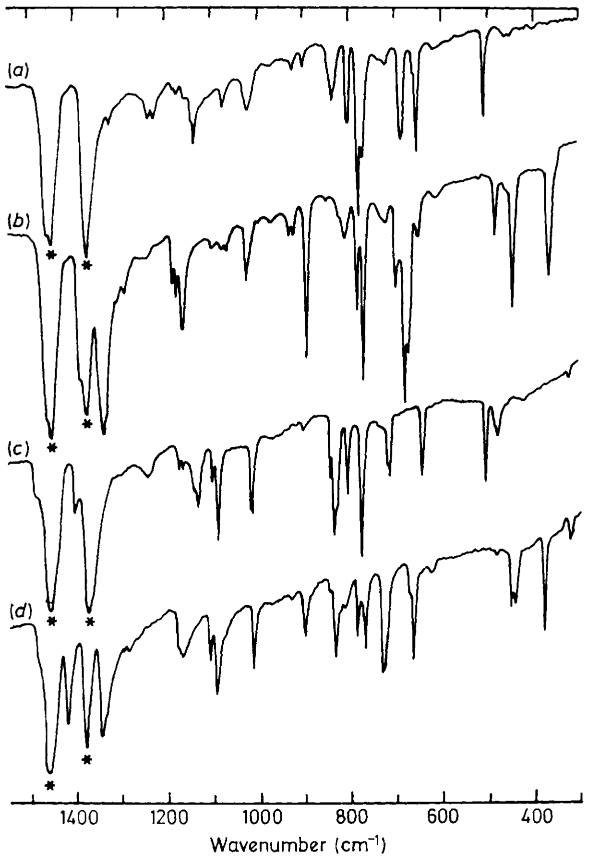


Figure 2. Comparison of i.r. spectra of $(PhCN_2S_2)_2$ and $(p\text{-}ClPhCN_2S_2)_2$ before [spectra (*a*) and (*c*)] and after [(*b*) and (*d*)] plasma nitrogenation. Nujol mulls, CsI plates; * indicates Nujol absorption bands

and the boat. Iodine was identified in the cold trap by i.r. and Raman spectroscopy. With X = Br$^-$ or CN$^-$ reaction occurred at 47 °C and was complete in about 12 h. Bromine in the cold trap was again identified spectroscopically, while the CN$^-$ anion was presumably incorporated into the polymeric co-product.

(4) *Preparation of* Bu^{t}CNSSN *from* [Bu^{t}CNSSN]$^+$Cl$^-$.—The compound [Bu^{t}CNSSN]$^+$Cl$^-$ (0.5 g, 2.5 mmol)[14] in liquid SO$_2$ was reduced with an excess of Zn–Cu couple. This was stirred for 6 h at room temperature after which the liquid SO$_2$ was carefully vented off into a vacuum line *via* a U tube held at −15 °C. After the SO$_2$ had evaporated, a warm water-bath was applied to the solid residue, with pumping. A dark red volatile liquid condensed in the connecting tubes and finally in the U tube. The product (0.33 g, 80% based on Bu^{t}CN$_2$S$_2$Cl) was a red-green solid which melted at room temperature to give a red paramagnetic liquid. Further purification was achieved by another fractional distillation [Found: C, 37.1; H, 5.5; N, 17.5; S, 40.0. $C_5H_9N_2S_2$ requires C, 37.2; H, 5.6; N, 17.4; S, 39.8%; mass spectrum (c.i.) *m*/*z* 161 $(C_5H_9N_2S_2)^+$, 61%, 64 $(S_2)^+$, 70%, and 57 (Bu^t)$^+$, 51%]. D.s.c. (4 °C min^{-1}): m.p. 22 °C.

(5) *Preparation of* PrCNSSN *from* [PrCNSSN]$^+$Cl$^-$.—The preparation of the starting chloride which has not been reported in the literature was carried out in a similar fashion to [PhCNSSN]$^+$Cl$^-$. The compound [PrCNSSN]$^+$Cl$^-$ (0.5 g, 2.7 mmol) was reduced in the same way as in (4) above. The product (0.26 g, 62%) was a red solid which melted to a red liquid on warming to room temperature [Found: C, 32.4; H, 4.6; N, 19.3; S, 44.1. $C_4H_7N_2S_2$ requires C, 32.6; H, 4.75; N, 19.0; S, 43.6%; mass spectrum (c.i.) *m*/*z* 147 $(C_4H_7N_2S_2)^+$, 57%, and 69 $(C_3H_7CN)^+$, 100%]. D.s.c. (4 °C min^{-1}): m.p. 10.0 °C.

(6) *Preparation of* (MeCNSSN)$_2$ (**5**) *from* [MeCNSSN]$^+$Cl$^-$ (**5′**).[15]—Compound (**5′**) (0.5 g, 3.2 mmol) was reduced in the same way as above. The product (0.34 g, 57%), which sublimed under dynamic vacuum into a U tube, was a very air- and moisture-sensitive red-green volatile solid (Found: C, 20.3; H, 2.6; N, 23.3; S, 53.6. $C_2H_3N_2S_2$ requires C, 20.1; H, 2.5; N, 23.5; S, 53.8%).

(7) *Reaction of* $(RCN_2S_2)_2$ *with a Nitrogen D.C. Plasma* (R = Pr *or* Bu^t).—Since at room temperature both these derivatives are liquids,[16] they are presumably largely present as free-radical monomers. The discharge apparatus was modified [Figure 1(*b*)] and since the d.c. nitrogen discharge occurs at low pressures, low temperatures were needed to cool the liquid. Typically 5 cm^3 of liquid were syringed into the bulb which was sealed in the glove-box. This was then removed and connected to the nitrogen line and the discharge apparatus. The whole bulb and side arm were then immersed in a cold bath cooled to −10 °C. With a nitrogen flow of 50 Torr cm^3 s^{-1} the discharge was ignited at a pressure of 1 Torr. At −10 °C a small amount of brown polymer formed on the walls of the discharge tube, whilst some red monomer collected in the cold trap. As the temperature was raised to 0 °C an increasing amount of polymer formed. After about 8 h there was no remaining liquid in the bulb and a dense coating of a brown film had formed which i.r. spectra revealed to be polymeric with broad ill defined absorptions.

(8) *Reaction of* $[RCN_2S_2]^+X^-$ (R = Pr *or* Bu^t, X = I *or* Br) *with a D.C. Nitrogen Discharge*.—Using the discharge tube in Figure 1(*b*), $[RCN_2S_2]^+X^-$ (0.5 g) was placed in the bulb and cooled to −5 °C. Using a flow rate of 50 Torr cm^3 s^{-1} and maintaining a current of 2.5 mA, the discharge was ignited. After 5 h the temperature was raised to 0 °C. The reaction was complete in a further 8 h. A heavy coating of polymer had formed on the discharge tube walls and the trapped halogen (I$_2$ or Br$_2$) was identified by i.r. and Raman spectroscopy.

(9) *Reaction of* [PhCNSSN][S$_3$N$_3$] (**8**) *with Nitrogen Plasma*.—4-Phenyl 1,2,3,5-dithiadiazolylium trithiatriazinide is a new compound that can be prepared by several methods, *e.g.* from [PhCNSSN][AsF$_6$] and [NPr$_4$][S$_3$N$_3$].[17] Compound (**8**) (0.030 g, 0.094 mmol) was exposed to the nitrogen plasma. The reaction proceeded without any additional heating (*i.e.* at *ca.* 35 °C inside the discharge tube) to give (**2**). A black polymer film formed on the tube wall.

(10) *Cyclic Voltammetry*.—All electrochemical measurements were carried out under strict exclusion of moisture and oxygen in a specially designed airtight three-limbed electrode cell described elsewhere.[18] Cyclic voltammograms were recorded using a Bioanalytical System Inc. CV-1B instrument and a Linseis LY17100 XY chart recorder. The working electrode was a platinum disc (0.002 cm^2) pressure molded in tetrafluoroethylene–hexafluoropropylene copolymer. The reference electrode used was Ag–Ag$^+$ (0.1 mol dm^{-3} AgBF$_4$, 0.2 mol dm^{-3} NBu$_4$BF$_4$ in MeCN); its potential *vs.* a saturated calomel electrode, +0.32 V, remained stable ±0.002 V over a period of several months. The solvent was acetonitrile doubly distilled over CaH$_2$ and finally passed through an alumina (Woelm B-super 1) column. All distillations and experiments were performed under an atmosphere of dry nitrogen.

Table 1. Bond lengths (Å) and angles (°) within $(MeCN_2S_2)_2$ molecules

S(11)–S(12)	2.077(1)	S(11)–N(11)	1.628(3)
S(12)–N(12)	1.639(3)	N(11)–C(11)	1.333(5)
N(12)–C(11)	1.329(4)	C(11)–C(12)	1.488(6)
S(21)–S(22)	2.071(2)	S(21)–N(21)	1.632(3)
S(22)–N(22)	1.636(4)	N(21)–C(21)	1.347(6)
N(22)–C(21)	1.326(5)	C(21)–C(22)	1.502(6)
S(31)–S(32)	2.078(2)	S(31)–N(31)	1.628(3)
S(32)–N(32)	1.639(3)	N(31)–C(31)	1.331(6)
N(32)–C(31)	1.323(5)	C(31)–C(32)	1.494(5)
S(41)–S(42)	2.074(1)	S(41)–N(41)	1.629(3)
S(42)–N(42)	1.636(3)	N(41)–C(41)	1.343(5)
N(42)–C(41)	1.313(4)	C(41)–C(42)	1.500(6)
S(51)–S(52)	2.074(1)	S(51)–N(51)	1.629(3)
S(52)–N(52)	1.639(3)	N(51)–C(51)	1.341(4)
N(52)–C(51)	1.326(5)	C(51)–C(52)	1.478(5)
S(61)–S(62)	2.084(2)	S(61)–N(61)	1.639(3)
S(62)–N(62)	1.641(4)	N(61)–C(61)	1.337(4)
N(62)–C(61)	1.322(6)	C(61)–C(62)	1.500(6)
S(71)–S(72)	2.078(2)	S(71)–N(71)	1.626(3)
S(72)–N(72)	1.629(4)	N(71)–C(71)	1.335(6)
N(72)–C(71)	1.328(5)	C(71)–C(72)	1.507(6)
S(81)–S(82)	2.074(2)	S(81)–N(81)	1.633(4)
S(82)–N(82)	1.635(4)	N(81)–C(81)	1.341(6)
N(82)–C(81)	1.327(5)	C(81)–C(82)	1.493(6)
S(12)–S(11)–N(11)	95.0(1)	S(11)–S(12)–N(12)	93.8(1)
S(11)–N(11)–C(11)	114.2(2)	S(12)–N(12)–C(11)	114.8(3)
N(11)–C(11)–N(12)	122.1(3)	N(11)–C(11)–C(12)	119.1(3)
N(12)–C(11)–C(12)	118.8(4)	S(22)–S(21)–N(21)	94.7(1)
S(21)–S(22)–N(22)	94.7(1)	S(21)–N(21)–C(21)	114.2(2)
S(22)–N(22)–C(21)	114.5(3)	N(21)–C(21)–N(22)	122.0(3)
N(21)–C(21)–C(22)	118.2(3)	N(22)–C(21)–C(22)	119.7(4)
S(32)–S(31)–N(31)	94.8(1)	S(31)–S(32)–N(32)	94.1(1)
S(31)–N(31)–C(31)	113.9(2)	S(32)–N(32)–C(31)	114.1(3)
N(31)–C(31)–N(32)	123.1(3)	N(31)–C(31)–C(32)	117.9(3)
N(32)–C(31)–N(32)	119.0(4)	S(42)–S(41)–N(41)	94.7(1)
S(41)–S(42)–N(42)	94.2(1)	S(41)–N(41)–C(41)	114.0(2)
S(42)–N(42)–C(41)	114.8(3)	N(41)–C(41)–N(42)	122.3(3)
N(41)–C(41)–C(42)	117.7(3)	N(42)–C(41)–C(42)	120.0(4)
S(52)–S(51)–N(51)	94.1(1)	S(51)–S(52)–N(52)	94.6(1)
S(51)–N(51)–C(51)	115.4(3)	S(52)–N(52)–C(51)	114.8(2)
N(51)–C(51)–N(52)	121.1(3)	N(51)–C(51)–C(52)	119.0(4)
N(52)–C(51)–C(52)	119.9(3)	S(62)–S(61)–N(61)	94.6(1)
S(61)–S(62)–N(62)	94.0(1)	S(61)–N(61)–C(61)	114.1(3)
S(62)–N(62)–C(61)	114.9(2)	N(61)–C(61)–N(62)	122.4(4)
N(61)–C(61)–C(62)	118.3(4)	N(62)–C(61)–C(62)	119.3(3)
S(72)–S(71)–N(71)	94.0(1)	S(71)–S(72)–N(72)	94.8(1)
S(71)–N(71)–C(71)	114.9(2)	S(72)–N(72)–C(71)	114.2(3)
N(71)–C(71)–N(72)	122.0(4)	N(71)–C(71)–C(72)	117.9(3)
N(72)–C(71)–C(72)	120.1(4)	S(82)–S(81)–N(81)	94.8(1)
S(81)–S(82)–N(82)	94.5(1)	S(81)–N(81)–C(81)	113.9(2)
S(82)–N(82)–C(81)	114.4(3)	N(81)–C(81)–N(82)	122.4(4)
N(81)–C(81)–C(82)	117.8(4)	N(82)–C(81)–C(82)	119.8(4)

Distances (Å) and angles (°) of MeCNSSN: averages of values pertaining to eight dithiadiazolium rings of the asymmetric unit.

S–S	2.076(2)	S–S–N	94.5(1)
S–N	1.636(3)	C–N–S	114.5(3)
N–C	1.324(5)	N–C–N	122.2(4)
C–C	1.495(6)	N–C–C	118.9(4)

Between two monomers:

S(1) ··· S(2) (av.) 3.097(3)

The supporting electrolyte, NBu_4BF_4, was prepared by metathesis from NBu_4HSO_4 (Labkemi AB, Sweden) and KBF_4 (BDH Ltd.), purified by double crystallisation from ethyl acetate–diethyl ether and finally vacuum dried (10^{-5} Torr) at 125 °C. All solutions and cells were prepared and sealed under nitrogen in a glove-box.

PhCNSNSN. The compound $PhCN_3S_2$ (0.0053 g, 0.014 mmol) was dissolved in dry CH_2Cl_2 (10 cm^3) and MeCN (5 cm^3) with tetrabutylammonium tetrafluoroborate (0.43 g, 1.3 mmol). Voltammograms run at +5.0 °C showed an oxidation half-wave potential ($E_{\frac{1}{2}}^{ox}$) at +1.3 V and a reduction half wave-potential ($E_{\frac{1}{2}}^{red}$) at −0.52 V.

(11) *Crystal Structure of* $(MeCNSSN)_2$, (**5**).—*Crystal growth.* A suitable crystal was isolated from a sealed Pyrex tube containing *ca.* 60 mg of (**5**) within which a random mass transport was driven by natural fluctuations of ambient temperature over a period of nearly a year. Numerous earlier attempts at growing crystals by controlled sublimation in experiments of shorter duration (hours or days rather than months) failed. In many instances the crystals grown were well shaped but their diffraction pattern invariably betrayed a highly imperfect lattice, mainly due to twinning and a heavy mosaic texture.

Crystal data. $C_4H_6N_4S_4$, $M = 238.4$, triclinic, space group $P\bar{1}$, $a = 11.296(1)$, $b = 12.498(1)$, $c = 14.647(2)$ Å, $\alpha = 72.06(1)$, $\beta = 77.85(1)$, $\gamma = 77.30(1)°$, $U = 1\,896.3$ Å^3, $Z = 8$, $D_c = 1.670$, $F(000) = 976$, $\lambda(Cu\text{-}K_\alpha) = 1.54\,184$ Å (graphite monochromator), $\mu = 8.74$ mm^{-1}, $T = 295$ K.

Intensity data from a crystal of dimensions 0.5 × 0.2 × 0.2 mm mounted under N_2 in a sealed quartz capillary were collected on a Siemens AED2 diffractometer (ω–θ scans with on-line profile fitting,[19] $2\theta_{max.}$ 130°, one unique hemisphere of data with $l > 0$; no significant variation for three standard reflections). Semiempirical absorption corrections were applied (transmission 0.11—0.27); 6 241 unique reflections were measured. For determination of the structure, 5 103 reflections were used, with $F > 4\sigma_c(F)$ (σ_c based on counting statistics only).

Structure determination.[20] All non-H atoms were located by direct methods and refined with anisotropic thermal parameters and with H atoms constrained to give C–H 0.96 Å, H–C–H 109.5°, and $U(H) = 1.2U_{eq}(C)$. Weights were assigned as $W^{-1} = \sigma^2(F) = \sigma_c^2(F) + 1 + 35G + 10G^2 - 6S + 6S^2 - 29GS$ ($G = F_o/F_{max.}$, $S = \sin\theta/\sin\theta_{max.}$).[21] An isotropic extinction parameter X was refined to $X = 5.3(4) \times 10^{-6}$, where $F_c' = F_c/(1 + X\,F_c^2/\sin 2\theta)^{\frac{1}{4}}$. Final residuals are $R = 0.040$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.060$, goodness of fit = 1.17; mean and maximum shift/error were 0.06 and 0.62, and all features in the final difference synthesis were between +0.16 and −0.33 e Å^{-3}. Atomic scattering factors were taken from ref. 22. Bond lengths and angles are given in Table 1, refined co-ordinates in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

The $(MeCN_2S_2)_2$ *Molecule.*—The dithiadiazole $(PhCNSSN)_2$ (**1**) previously described[8] crystallises in an eclipsed conformation with two S ··· S interactions between the rings. In contrast, isoelectronic $[S_6N_4]Cl_2$ has a *trans* arrangement of the two rings, thereby minimising anion–anion repulsions. The compound $[CF_3CNSSN]_3Cl$ crystallises as a combination of $[CF_3CNSSN]^+Cl^-$, with the chloride coplanar with the ring, and the dimer $(CF_3CNSSN)_2$ with eclipsed rings [as in $(PhCN_2S_2)_2$].

MNDO calculations[23] have, in fact, shown that for most dithiadiazole derivatives the energy difference between the two conformations is only very small, about 5 kJ mol^{-1}.

The methyl derivative, like (**1**), contains parallel rings within

Table 2. Final atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S(11)	3 900(1)	6 118(1)	4 352(1)	S(51)	3 755(1)	6 302(1)	2 075(1)
S(12)	5 532(1)	6 758(1)	4 036(1)	S(52)	4 358(1)	5 763(1)	825(1)
N(11)	3 462(2)	6 414(2)	5 392(2)	N(51)	5 120(2)	6 031(2)	2 377(2)
N(12)	5 303(2)	7 108(2)	5 058(2)	N(52)	5 801(3)	5 413(2)	985(2)
C(11)	4 251(3)	6 895(3)	5 630(2)	C(51)	6 029(3)	5 612(3)	1 765(2)
C(12)	3 935(4)	7 232(4)	6 553(3)	C(52)	7 302(3)	5 363(4)	1 971(3)
S(21)	2 686(1)	8 491(1)	3 193(1)	S(61)	4 082(1)	8 763(1)	860(1)
S(22)	2 182(1)	8 949(1)	4 482(1)	S(62)	5 874(1)	8 400(1)	1 159(1)
N(21)	3 992(2)	8 960(2)	2 908(2)	N(61)	4 459(3)	8 389(2)	−156(2)
N(22)	3 435(3)	9 462(2)	4 371(2)	N(62)	6 467(3)	8 002(3)	167(2)
C(21)	4 221(3)	9 405(3)	3 569(3)	C(61)	5 664(3)	8 049(3)	−389(3)
C(22)	5 431(4)	9 804(3)	3 399(4)	C(62)	6 102(4)	7 659(4)	−1 293(3)
S(31)	1 106(1)	3 549(1)	6 260(1)	S(71)	999(1)	8 055(1)	1 336(1)
S(32)	−549(1)	3 564(1)	5 846(1)	S(72)	−683(1)	8 066(1)	968(1)
N(31)	1 567(3)	2 184(2)	6 421(2)	N(71)	1 568(3)	6 778(3)	1 228(2)
N(32)	−277(3)	2 194(2)	5 936(2)	N(72)	−309(3)	6 798(3)	799(2)
C(31)	780(3)	1 657(3)	6 232(2)	C(71)	815(3)	6 280(3)	964(2)
C(32)	1 132(4)	405(3)	6 339(3)	C(72)	1 292(4)	5 106(4)	826(4)
S(41)	2 389(1)	3 916(1)	4 072(1)	S(81)	1 936(1)	9 222(1)	−762(1)
S(42)	2 767(1)	2 171(1)	4 248(1)	S(82)	2 513(1)	7 636(1)	−1 025(1)
N(41)	1 075(3)	4 093(2)	3 708(2)	N(81)	576(3)	9 406(3)	−1 058(2)
N(42)	1 498(2)	2 137(2)	3 894(2)	N(82)	1 222(3)	7 614(3)	−1 351(2)
C(41)	778(3)	3 128(3)	3 666(2)	C(81)	373(3)	8 530(3)	−1 318(2)
C(42)	−434(4)	3 205(4)	3 364(3)	C(82)	−869(4)	8 592(4)	−1 551(3)

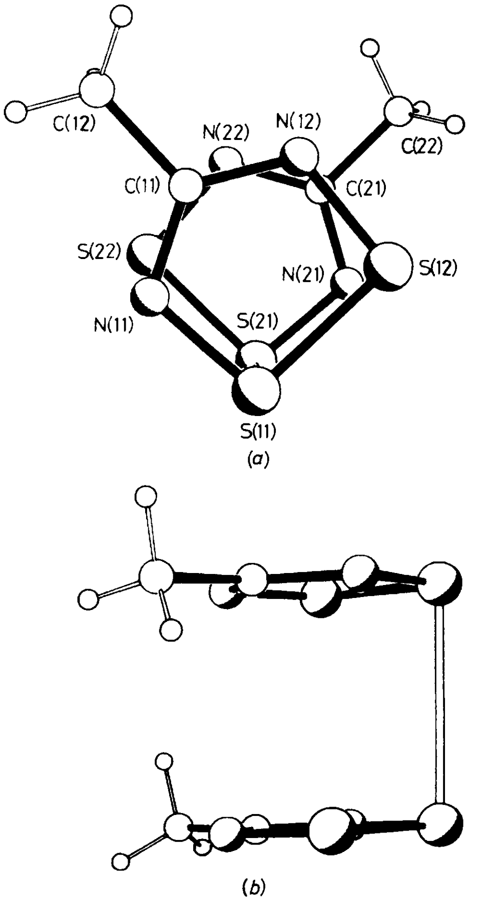


Figure 3. The $(MeCN_2S_2)_2$ molecule viewed approximately (*a*) along the S(11)–S(21) bond, (*b*) perpendicular to the S(11)–S(21) bond

the dimer unit (see Figure 3). However, there is only one S $\cdots$ S link of 3.108 Å between the rings. There are also weak S $\cdots$ N and S $\cdots$ S secondary interactions between adjacent dimer units (typically 3.0 Å). When the lattice is viewed parallel to the *a* axis the crystal appears composed of 'sheet polymers' parallel to the (011) plane, completely interwoven by dimer–dimer close van der Waals contacts concentrated around the central plane of the sheet while the methyl groups are pointing away from the central plane. This stacking arrangement thus creates a periodicity of high- and low-density regions as well as relatively weak bonding between the polymer layers. This in turn accounts for an easy glide movement in the (011) plane and the pronounced tendency for twinning.

The C–N, S–N, and S–S bond distances within each ring differ very little from those found in compound (**1**) except for the S $\cdots$ S inter-ring interaction which is slightly longer in the methyl case (3.108 against 3.08 Å), possibly due to steric factors. The difference, however, is probably negligible. In fact apart from the S $\cdots$ S inter-ring distances which do vary appreciably, the R substituent appears to have very little effect on the S–C–N ring distances and angles.

The Plasma Reactions.—We have previously reported[3] the unique insertion of atomic nitrogen, generated in a d.c. plasma, into the disulphide link of the five-membered 1,2-dithiadiazole RCN_2S_2 (R = Ph or *p*-ClC_6H_4).

We now discuss these reactions in more detail and analogous reactions with RCN_2S_2 (R = Me, Pr, or Bu^t) and with $[RCN_2S_2]^+X^-$ (R = Ph, *p*-ClC_6H_4, Pr, or Bu^t; X = Cl, Br, or I). Structural criteria which facilitate the nitrogenation reaction are discussed with particular regard for $(MeCN_2S_2)_2$ for which the *X*-ray data are given.

In general, plasmas contain electronically excited ions and atoms and vibrationally and electronically excited molecules. Spectroscopic studies have identified a number of species in nitrogen discharges,[24] and the more exotic ones, *e.g.* N_4^+, still attract attention.[25] However, the main species is the ground-state nitrogen atom (^4S), from the dissociation of N_2, which lies at 12.139 eV.[26] The ^4S nitrogen atoms are the chemically active species[27] in free-radical active nitrogen reactions. Electronically excited atoms and molecules and vibrationally excited molecules have a lower concentration and the longest-lived excited state, the $A^3\Sigma_u^+$ state, has a lifetime of only 10^{-2} s.

Furthermore at these relatively high pressures ($p \approx 2$—4 Torr) ^4S nitrogen atoms tend to quench the other excited atoms, *e.g.*, $N(^2P) + N(^4S) \longrightarrow 2N(^4S)$.

In this work we have assumed that an equilibrium between ^4S nitrogen and N_2 molecules is maintained whilst the discharge continues and that the chemically active species are ^4S nitrogen atoms. From studies of the afterglow,[24] it has been found that the $N(^4S)$ atoms have a relatively long lifetime due to their decay being a three-body recombination, although catalytic decay does take place at surfaces: $N + N + M \longrightarrow N_2 + M$ (M = a neutral molecule). For this process $-d[N]/dt = 2k[N]^2[M]$ and the rate k is 2.1×10^{-32} cm^6 molecule^{-1} s^{-1}.[24]

Ionisation also takes place in plasmas but the reports[24] of the degree vary enormously from 0.1 to 100% and it to some extent depends on how the discharge is generated. However, because of the large amount of u.v. radiation given off in a d.c. discharge it has been inferred that vibrationally excited molecules may also take part in some chemical reactions. We therefore carried out an experiment under identical conditions, but instead of igniting the discharge the sample and the tube were irradiated with high energy (6.5 eV and above) u.v. light to stimulate the formation of vibrationally excited N_2. This was also repeated under static conditions and in both instances no uptake of nitrogen was observed; the sample remained unchanged. It is concluded therefore that the reactions primarily involve atomic ^4S nitrogen and not vibrationally excited N_2 molecules.

MNDO calculations[23] and e.s.r. studies have indicated that the odd electron in $PhCN_2S_2$ lies in a singly occupied molecular orbital (s.o.m.o.) distributed over the NSSN fragment of the ring and dimerisation occurs through σ overlap of the z components at the sulphurs. Figure 4 shows the s.o.m.o. and dimer structure.[27] Our own MNDO calculations show that, perpendicular to the ring, the p-orbital contributions at sulphur and nitrogen are roughly 1 : 1. Further, e.s.r. studies have shown $PhCN_2S_2$ to consist largely of dimer units in the solid state, but with a very small proportion (< 1%) of monomer radical present. The percentage of monomer in alkyl derivatives (where R = Pr or $\mathrm{Bu^t}$) rises considerably such that for $\mathrm{Bu^t}$ at room temperature the majority (> 75%) consists of monomer.[28]

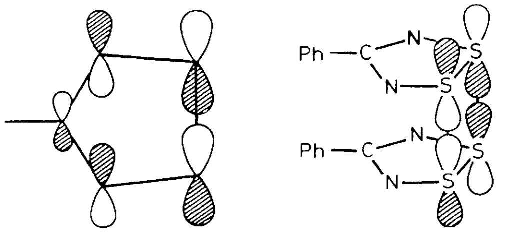
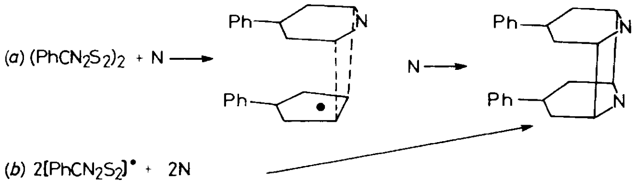


Figure 4. Diagramatic representation of the s.o.m.o., and the overlap of the P_z component in the $(PhCN_2S_2)_2$ dimer unit

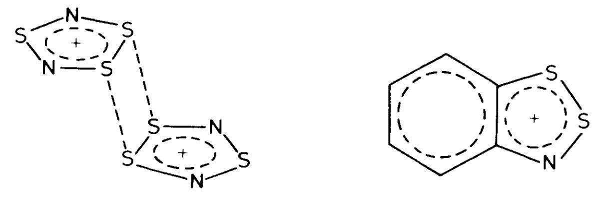
For the group of compounds RCN_2S_2 where R = Pr or $\mathrm{Bu^t}$ which are liquids at room temperature the apparatus was slightly modified and used at −30 to +40 °C [see Figure 1(*b*)]. However, the major product was again a brown non-conducting C/N/S non-stoicheiometric polymer.

The dithiadiazole may react in two possible ways (Scheme 1): as the monomer with atomic nitrogen in a radical–radical reaction (*b*), or in the dimer form (*a*). The latter is more likely because of the very low concentration of monomer present in the solid, though reaction *via* the monomer must take place to some extent.

X-Ray crystal structure studies[8] have shown that for $(PhCN_2S_2)_2$ there are channels running parallel through the lattice. These have a diameter of in excess of 3.5 Å [see Figure 5(*d*)]; the atomic radius of atomic nitrogen is 1.3 Å, so that it is possible for atomic nitrogen to diffuse through the crystal structure to the reaction sites. Whole crystals when subjected to plasma nitrogen showed very definite reactant/product boundaries which were observed to move with time and so the solid-state reaction may well be diffusion controlled.



Scheme 1.



Scheme 2.

As expected, the ease of chemical and electrochemical reduction of $[RCN_2S_2]^+X^-$ increases with the atomic number of the halogen, X. Consequently, the various halides (X = Cl, Br, or I) of both the aryl and the alkyl derivatives were all subjected under similar conditions to a nitrogen d.c. plasma discharge. For the aryl derivatives, it was observed that the chlorides were inactive but that the bromides and the iodides both yielded the same product $\mathrm{R\overline{CNSNSN}}$ (R = aryl) with release of halogen. As expected, the iodides required the lower reaction temperatures.

In the case of the alkyl derivatives, however, the corresponding halogen was again released, but with almost complete conversion into a brown polymer. Presumably because their radicals are monomeric, the alkyl derivatives are too volatile and are quickly lost into the gas phase where they are subjected to the vigorous conditions of the plasma with consequent molecular fragmentation and conversion into a non-stoicheiometric polymer. Thus no compounds RCN_3S_2 (R = alkyl) were obtained from the cations and free radicals, only non-stoicheiometric polymer. The polymers obtained from both aryl- and alkyl-dithiadiazoles were all air stable, and adhered strongly to the surface of the quartz boat and glass discharge tube.

The mechanism of these nitrogen-insertion reactions involving dithiadiazolium salts is uncertain. However, for the cation reactions the most likely first step is the electron transfer to give the neutral radical $\mathrm{R\overline{CNSSN}}^{\bullet}$. This electron may either come from the pool of free electrons in the plasma or from the anion through bombardment with the nitrogen atoms (which would explain the correlation between reactivity and the ionisation potential of the halide ion). Clearly the energies required for the ionisation of X^-, the reduction of $RCN_2S_2^+$, as well as for molecular/lattice reorganisation and bond formation must have their source in the plasma.

A further contributory factor to the ease of the reaction of the cations, however, must be the high electron affinity. Since the lowest unoccupied molecular orbital (l.u.m.o.) of $[\mathrm{R\overline{CNSSN}}]^+$ is antibonding with respect to both the SS bond and the SN bonds the first electron provision will weaken both bond types. Formation of the new S–N bond (stronger than the S–S bond replaced, 264 kJ mol^{-1}; 243 kJ mol^{-1} for single S–N bond or 301 kJ mol^{-1} for bond order 1.5)[29] completes the process.

Further S/N compounds were also subjected to plasma nitrogen including S_8, S_4N_4, $[S_3N_2Cl]Cl$, and $[S_4N_3]Br$. It was thought that, in particular, the structural similarities of S_3N_2Br

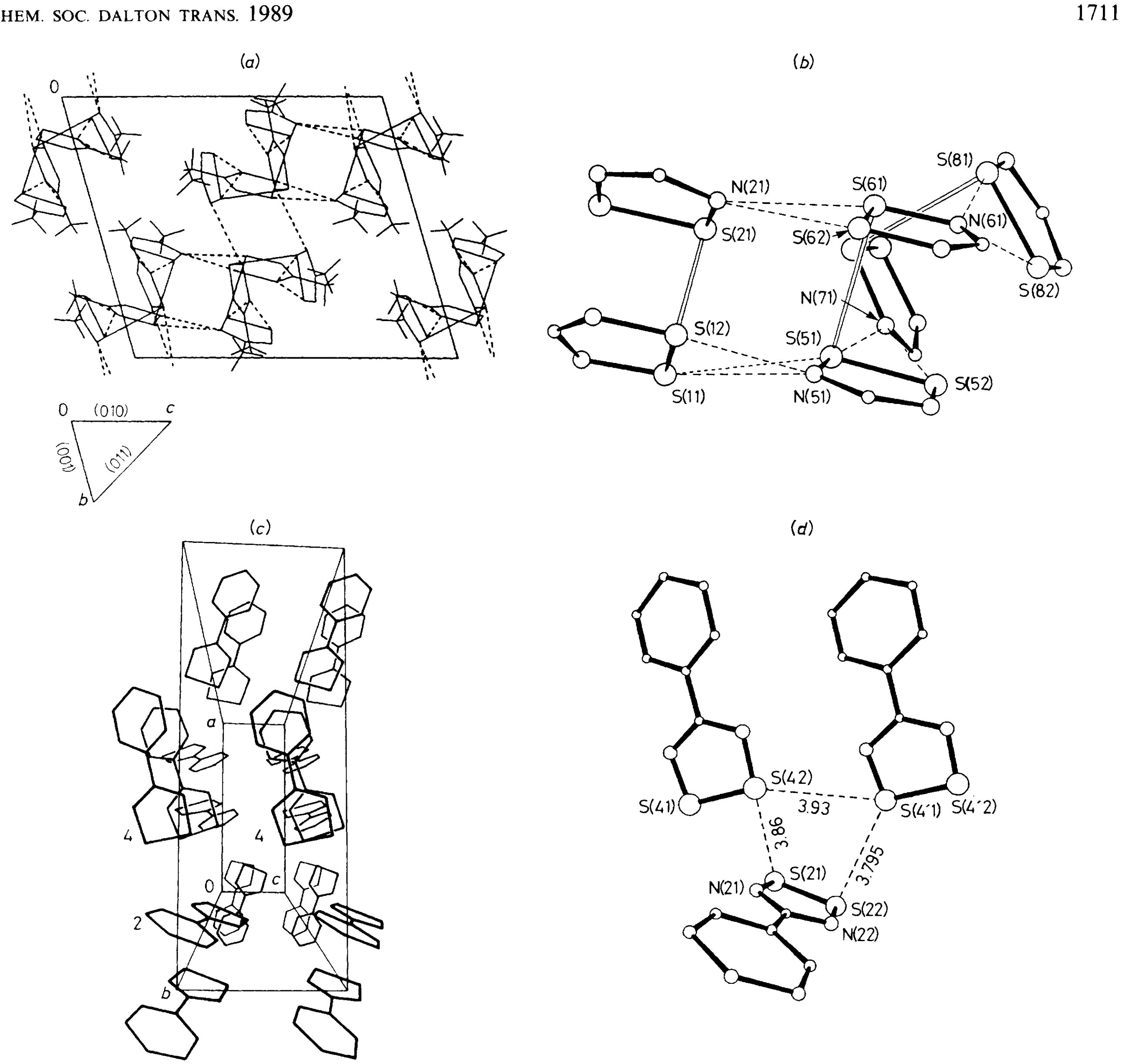


Figure 5. Comparison of the $(MeCN_2S_2)_2$ and $(PhCN_2S_2)_2$ crystal structures. (*a*) 'Stick model' projection of the $(MeCN_2S_2)_2$ structure parallel to the *a* axis with the close S···N intermolecular contacts shown as dashed lines. (*b*) Three neighbouring $(MeCN_2S_2)_2$ 'dimer' molecules showing the close S···N and S···S contacts between them (dashed lines). The projection direction is the same as in (*a*); the methyl groups are omitted for clarity. The long S–S bond between two cofacial five-membered rings (referred to as 'dimer') are drawn as double lines. The distances are: S(11)···S(21) 2.954, S(51)···S(61) 3.036, S(11)···S(51) 2.954, S(11)···N(51) 2.954, S(12)···N(51) 2.995, S(51)···N(71) 2.861, S(52)···N(71) 3.132, S(61)···N(21) 3.063, S(62)···N(21) 3.120, S(81)···N(61) 3.032, and S(82)···N(61) 3.182 Å. (*c*) A perspective view down the *b* axis (32.98 Å) of the $(PhCN_2S_2)_2$ orthorhombic unit cell, showing the van der Waals channels [*cf.* (*d*)]. Only the molecules filling the upper half of the unit cell are shown. (*d*) The 'bottle-neck' of the channels with the S···S distances shown [corresponding to positions of three of the $(PhCN_2S_2)_2$ molecules in (*c*), numbered 2, 4, and 4′]

or $C_6H_4NS_2{}^+Br^-$ (Scheme 2) would facilitate the insertion of nitrogen. Other SS bonded species such as $[S_4N_3]Br$ and various transition-metal complexes containing the disulphide group such as $[Ti(\eta^5\text{-}C_5H_5)_2(S_7)]$ and $[Pt(N_2HS_2)(PPh_3)]\text{-}BF_4$* were also placed in a nitrogen discharge. In all these cases, however, the sample was either left unchanged or, particularly in the case of the sulphur-rich compounds, varying amounts of $(SN)_x$ were obtained as thin films coating the walls of the discharge tube.

The compound $[\text{Ph}\overline{\text{CNSSN}}][S_3N_3]$ which, like (**1**) contains adjacent $PhCN_2S_2$ units, did react with atomic nitrogen to yield $(PhCN_3S_2)_2$ and at a much lower temperature than previously observed for (**1**); the reaction occurred readily at room temperature. There was no $(SN)_x$ observed or other sulphur compounds which could be expected from the fragmentation of the S_3N_3 unit. It is concluded therefore that all the S/N from this is incorporated in the black C/S/N polymer layer which also forms.

$PhCN_3S_2$: *Cyclic Voltammetry and Reactions.*—The compound $(PhCN_3S_2)_2$ is air stable and rather chemically unreactive: this stability is also reflected in the high oxidation potential, found experimentally: $(PhCN_3S_2)_2 \longrightarrow$

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* Compounds kindly supplied by Dr. J. D. Woollins, Imperial College, London.

$2(\mathrm{PhCN_3S_2})^+ + 2e^-$; $E_{\frac{1}{2}} = +1.3$ V. A reduction peak was also found with value of -0.52 V. Neither of these two processes is reversible, suggesting that the cation and the anion of $\mathrm{PhCN_3S_2}$ are unstable. This is borne out experimentally, since although it is possible to obtain the cation and dication in solution with highly polar solvents, they are always associated with cationic polymer and further attempts to isolate the solid have so far resulted only in further polymerisation.

The dichloride derivative, $\mathrm{PhCN_3S_2Cl_2}$,[11] previously synthesised by the chlorination of $\mathrm{PhCN_5S_3}$, can easily be prepared in pure form by the reaction of sulphuryl chloride with $\mathrm{PhCN_3S_2}$. The chlorine atoms are readily replaced by other groups.

Of the 1,2,3,5-dithiadiazoles ($\mathrm{RCN_2S_2}$) studied, it was only in the case of R = Ph or *p*-$\mathrm{ClC_6H_4}$ that the plasma nitrogenation produced the corresponding 1,3,2,4,6-dithiatriazine ($\mathrm{RCN_3S_2}$). Our experimental results indicated several general criteria for successful nitrogen insertion into 1,2,3,5-dithiadiazoles.

(1) Since the reaction is heterogeneous (gas/solid), it is most likely controlled by the diffusion rate of the nitrogen atoms through the solid to the reaction sites.

(2) The crystal packing must be such as to permit diffusion of atomic nitrogen, whilst the packing itself is dependent on the substituent R in $\mathrm{RCN_2S_2}$. The substituent also has a profound effect on the stability of the produced intermediate and final product. When R = aryl the dithiadiazole and the dithiatriazine product are dimeric and the proposed intermediate is then a mixed five-membered/six-membered ring dimer. If, on the other hand, R = alkyl where the starting dithiadiazole, as a volatile liquid, is largely monomeric then the intermediates may also be monomeric, with consequential increased volatility and lack of dimeric stabilisation.

(3) The starting material and product must be solids of low volatility and sufficiently stable in the plasma. The experimental evidence suggests that when the temperature is high enough to generate vapour at a partial pressure comparable to that of the nitrogen in the plasma tube, polymeric films form on the reactant sample and on the discharge tube walls. This clearly is the case when R = alkyl (Pr or $\mathrm{Bu^t}$), even at below room temperature.

These criteria impose quite severe constraints both on suitable reactants and on reaction conditions. In an effort to ascertain just how restrictive these constraints were, we studied two special cases with similar physical properties: $(\mathrm{PhCN_2S_2})_2$ (**1**) and $(\mathrm{MeCN_2S_2})_2$ (**5**). Both (**1**) and (**5**) are dark green/purple bichromic crystalline dimeric solids at room temperature; both melt without decomposition, (**1**) at 121 °C and (**5**) at 95.5 °C. The vapour pressure of compound (**5**) was measured in this laboratory.[14] Unfortunately there are no vapour pressure/temperature data for (**1**), but from its very low sublimation rate in vacuum at the typical nitrogenation temperature of 45 °C we estimate it as between 0.01 and 0.1 Torr.

As mentioned above, support for a diffusion-controlled mechanism for the nitrogenation of compound (**1**) was obtained by examining the cross-section of a single crystal at various stages of the plasma reaction. The different colours of the reactant and product made it easy to discern the boundary between the unreacted core of (**1**) and the surrounding buff coloured layer of $(\mathrm{PhCN_3S_2})_2$.

While the nitrogenation of (**1**) proceeded with a readily observable rate at 25 °C, an increment of just 20 °C produced a steep rise in the reaction rate. [Diffusion coefficient as a function of temperature is given by the Arrhenius relation $D = D_0 \exp(-E_d/kt)$, where E_d is the activation energy of diffusion and D_0 is the frequency or pre-exponential factor.]

In contrast to compound (**1**) there was no analogous formation of $(\mathrm{MeCN_3S_2})_2$ from (**5**) over a range of temperature (-25 to $+50$ °C). A likely reason for this becomes clear from a comparison of the molecular packing in the crystal lattices of (**1**) and (**5**). While the structure of (**1**) has been known for some time,[8] it has not previously been possible to obtain crystals of (**5**). Figure 5 juxtaposes the molecular packing in the structures of (**1**) and (**5**). A perspective view down the *b* axis of the orthorhombic unit cell ($P2_12_12_1$) of (**1**) reveals sizeable van der Waals regions (channels) through which atomic nitrogen can reach the S $\cdots$ S links. The structure of (**5**) [Figure 5(*a*) and (*b*)] is best represented as a projection parallel to the *a* axis to reveal the close S $\cdots$ S and S $\cdots$ N contacts between adjacent dimer units.

Here, the units numbered 1—2 and 5—6 form a close contact of 2.954 Å between S(11) and S(51), shorter than the average distance of 3.100 Å between the sulphur atoms of the opposite coplanar rings. Thus, this type of packing leaves too small van der Waals regions between the S–S ends for effective N diffusion to occur. In addition to this adverse geometric factor the diffusion will be hampered by a lower temperature in the plasma tube necessitated by a higher vapour pressure of compound (**5**) with respect to (**1**).

Both the geometry and the reaction temperature considerations have dealt with the kinetic aspects. It is, however, possible that an important contributory factor to the successful plasma nitrogenation of (**1**) is the stabilisation energy which arises from a weak overlap of the uppermost π orbitals of the two cofacial $\mathrm{PhCN_3S_2}$ rings.[11] This is reflected in the considerably shorter distances, *viz.* 2.53 Å between the sulphur atoms of the two cofacial rings in $(\mathrm{PhCN_3S_2})_2$ as compared with an average distance of 3.11 Å of the dimeric $(\mathrm{PhCN_2S_2})_2$.

There is yet another kinetic advantage to be considered, namely the 'least motion' principle. The relatively minor spatial reorganisation occurring during the conversion of compound (1) into (2) results in a high degree of crystallinity of the product (as obtained by plasma nitrogenation at 45 °C). This crystallinity is seen from the well resolved sharp *X*-ray powder diffraction lines. In contrast, chemically prepared (2) according to Boeré gave fewer diffused lines probably due to a high degree of subdivision. Similar differences in the resolution quality apply to the i.r. spectra.

We conclude that the uniqueness of the plasma nitrogenation of $(\mathrm{Ph\overline{CNSSN}})_2$ and $(p\text{-}\mathrm{ClC_6H_4\overline{CNSSN}})_2$ arises from an unusual combination of a number of structural and volatility factors not easily matched by other related compounds. This study may help in identifying other compounds suitable for further nitrogen fixation studies.

Acknowledgements

Our gratitude goes to the S.E.R.C. for financial support (to A. J. B., W. C., and Z. V. H.) and for a studentship (to M. I. H.), and to I.C.I. for a studentship (to S. T. W.).

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Received 19*th September* 1988; *Paper* 8/03550D