Novel S–N Ring Contractions using the 4-Phenyl-1,2,3,5-dithiadiazole Dimer, the Synthesis and *X*-Ray Crystal Structures of [$(PhCN_2S_2)_2Cl$][S_3N_3], [$PhCN_2S_2$][S_3N_3], and [$PhCN_2S_2$][S_3N_2]Cl,† and an *Ab Initio* Molecular-orbital Study of the Bonding in [$PhCN_2S_2$][S_3N_3]

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When the 4-phenyl-1,2,3,5-dithiadiazole dimer (**1**) dehalogenates [S_5N_5]Cl a novel ring contraction occurs producing [$(PhCN_2S_2)_2Cl$][S_3N_3], (**2**), in acetonitrile, and a mixture of (**2**) and [$PhCN_2S_2$][S_3N_3], (**3**), in pentane. The salt [S_4N_3]Cl is also dehalogenated by (**1**) in acetonitrile giving [$PhCN_2S_2$][S_3N_2]Cl, (**4**). The *X*-ray crystal structures of (**2**)—(**4**) provide an insight into the electronic state of the CN_2S_2 rings in these three compounds by comparison of the S–S bond length with the known lengths in compound (**1**), [$PhCN_2S_2$][AsF_6], and [$PhCN_2S_2$]Cl. Extended-Hückel and *ab initio* molecular-orbital calculations were carried out on compound (**3**) and high-yield preparations of (**2**)—(**4**) are also described. The reactions of [S_5N_5]Cl or [S_4N_3]Cl with (**1**), in acetonitrile, produced in both cases the new e.s.r.-active compound [$PhCN_2S_2$]$_2$Cl, whose solid-state preparation is described. The reaction between the vapours of $(SN)_x$ and (**1**) produced (**3**) providing further evidence for $S_3N_3^{\bullet}$ being the major vapour-phase species above $(SN)_x$ *in vacuo* at *ca.* 160 °C.

The 4-phenyl-1,2,3,5-dithiadiazolylium ring system was first prepared[1] in 1977 as the chloride, and since then salts of many other anions have been reported.[2–6] Reduction of the chloride[6] affords the 4-phenyl-1,2,3,5-dithiadiazole dimer, which we have recently reported[7] to react with [S_5N_5]Cl and [S_4N_3]Cl to produce [$(PhCN_2S_2)_2Cl$][S_3N_3] and [$PhCN_2S_2$][S_3N_2]Cl by novel rearrangements involving dechlorination and ring contraction. We now report these novel ring contractions in more detail and also related syntheses. The unusual S $\cdots$ S interactions are discussed with the aid of *X*-ray data and molecular-orbital calculations.

Experimental

All manipulations of solids were performed in an atmosphere of dry nitrogen in a Vacuum Atmospheres Corporation glove-box (HE43-2) fitted with an HE943 Dri-Train. Reactions were either carried out in a previously described two-bulbed vessel[8] [Figure 1(*a*)], with each bulb being surmounted by a J. Young tap and separated by a glass sinter (no. 3), or in a specially designed sublimation apparatus [Figure 1(*b*)].

The dithiadiazole dimer $(PhCN_2S_2)_2$ (**1**) was prepared by Zn–Cu couple reduction of [$PhCN_2S_2$]Cl in tetrahydrofuran, followed by sublimation. The salt [S_5N_5][$AlCl_4$] was obtained[9] from the reaction between S_4N_4, $(NSCl)_3$ and $AlCl_3$ in $SOCl_2$, [S_5N_5]Cl[10] from the reaction between [S_5N_5][$AlCl_4$] and tetrahydrofuran, [S_4N_3]Cl[11] from the reaction between $S_3N_2Cl_2$ and SCl_2 in CCl_4, and [S_3N_2Cl][$FeCl_4$][12] from the reaction between $S_3N_2Cl_2$ and $FeCl_3$ in $SOCl_2$. The polymer $(SN)_x$ was obtained[13] from the solid-state polymerisation of S_2N_2 over a period of 8 weeks. The salt $AgAsF_6$ was obtained[14] from the reaction between silver and AsF_5 in SO_2.

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. Acetonitrile (h.p.l.c. grade) was refluxed over calcium hydride for 1 h and then distilled and stored in a sealed flask under an atmosphere of dry nitrogen. Pentane was stored over sodium wire without prior purification.

Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer 577 spectrometer, mass spectra on a VG Analytical 7070E spectrometer using the electron-impact (e.i.) mode. Differential scanning calorimetry (d.s.c.) was carried out with a Mettler FP85 thermal-analysis cell coupled with a FP80 central processor. Samples were cold-sealed in aluminium capsules.

Cyclic voltammograms were recorded using a potential-wave generator (type CV-1B; Bioanalytical Systems Inc., W. Lafayette, Indiana) and a Linseis *x-y* recorder (type LY 17100).

All molecular orbital (m.o.) calculations were carried out on a Digital VAX 6210 computer; further details are given in the Results and Discussion section.

Carbon, H, and N analyses were carried out on a Carlo Erba 1106 elemental analyser. Fluorine was determined by overnight fusion with potassium metal in a bomb, followed by passing the solution through an ion-exchange column [Amberlite resin IR-120(H)] and titrating against aqueous NaOH. Following oxygen-flask combustion, sulphur was determined as sulphate and chlorine as chloride by titration against barium perchlorate

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† Bis(4-phenyl-1,2,3,5-dithiadiazolylium) chloride 1,3,5,2,4,6-trithiatriazinide, 4-phenyl-1,2,3,5-dithiadiazolylium 1,3,5,2,4,6-trithiatriazinide, and 4-phenyl-1,2,3,5-dithiadiazolylium–1,2,4,3,5-trithiadiazole chloride respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. units employed: Torr ≈ 133 Pa, a.u. ≈ 5.29 × 10^{-11}m, cal = 4.184 J.

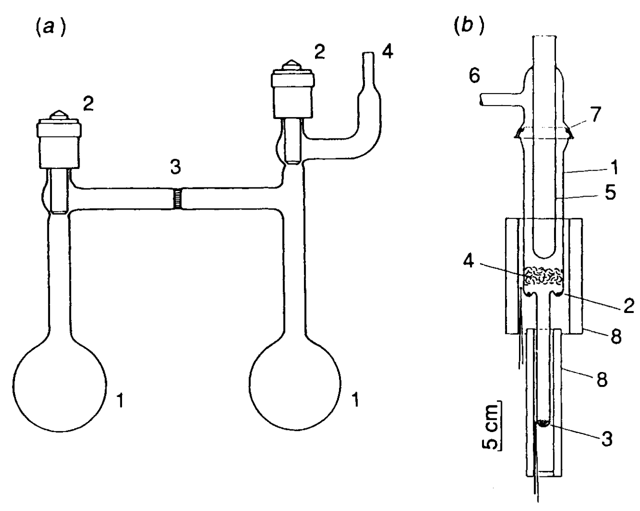


Figure 1. (*a*) Two-bulb reaction vessel: (1) reaction bulb, (2) J. Young Teflon-stemmed greaseless vacuum tap, (3) Pyrex sinter (usually porosity grade 3), and (4) outside diameter, $\frac{1}{4}$-in tubing for coupling to vacuum line using a $\frac{1}{4}$-in 'Swagelok' union with Teflon ferrules. (*b*) Sublimation apparatus for mixing the vapours of $(SN)_x$ and $(PhCN_2S_2)_2$: (1) two-tier sublimation tube, (2) upper tier in shape of an annular groove, containing $(SN)_x$ crystals at 160 °C, (3) bottom tier, containing $(PhCN_2S_2)_2$ crystals at 50 °C, (4) mixing–reaction zone filled with lightly compacted quartz wool (Thermal Syndicate, Ltd., type A), (5) cold-finger, (6) connection to a high vacuum unit, (7) J. Young greaseless ball joint, and (8) transparent resistance furnaces with control thermocouples

and silver nitrate respectively. Arsenic was determined by decomposition in acid and the concentration measured by atomic absorption spectrophotometry.

Crystal Growth of $[(PhCN_2S_2)_2Cl][S_3N_3]$ (**2**).—The salt $[S_5N_5]Cl$ (0.200 g, 0.75 mmol) was placed in one bulb of a two-bulb reaction vessel with $(PhCN_2S_2)_2$ (0.150 g, 0.41 mmol) in the other bulb. Acetonitrile (8 cm^3) was added to each side. Inversion of the reaction vessel allowed the solutions to mix by slow diffusion through a medium-porosity glass sinter. Removal of the brown solution (by syringe and pumping) yielded a few orange crystals of $[PhCN_2S_2]Cl$ and of S_4N_4, some black needles of $[PhCN_2S_2]_2Cl$ (**7**), and many large, golden, well faceted crystals of (**2**) in the $[S_5N_5]Cl$ compartment.

Crystal data. $C_{14}H_{10}ClN_7S_7$, $M = 536.2$, triclinic, space group $P\bar{1}$. $a = 9.509(2)$, $b = 10.641(2)$, $c = 12.187(3)$ Å, $\alpha = 98.29(1)$, $\beta = 107.61(1)$, $\gamma = 112.08(1)°$, $U = 1\,041.7$ Å^3, $Z = 2$, $D_c = 1.709$ g cm^{-3}, $F(000) = 544$, $\mu(Mo\text{-}K_\alpha) = 0.88$ mm^{-1}, $\lambda = 0.710\,73$ Å, crystal size 0.2 × 0.4 × 0.7 mm, in Lindemann capillary, $T = 295$ K.

Stoe-Siemens diffractometer, 32 reflections (2θ 20—25°) for cell refinement. Data collection by ω—θ scan, range 0.85 ° below α_1 to 0.85 ° above α_2, scan time 17.5—52.5 s, $2\theta_{max.} = 50$ °, h −11 to 11, k −12 to 12, l 0 to 14 plus a partial equivalent set with h 3 to 11, k −12 to 12, l −14 to 0. Three standard reflections, no significant variation. No absorption or extinction correction. 5 318 Reflections measured, 3 698 unique, 2 836 with $F > 4\sigma_c(F)$ (σ_c from counting statistics), $R_{int} = 0.012$. Structure solution by direct methods and difference synthesis (SHELXTL programs),[15] blocked-cascade least-squares refinement on F. $R = 0.038$, $R' = 0.039$, 262 parameters, mean shift/e.s.d. = 0.001, maximum = 0.003, largest peak in difference map +0.47, largest hole −0.35 e Å^{-3}, goodness of fit 1.08 with weighting scheme[16] $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 1 + 12G + 79G^2 - S + S^2 - 32GS$ ($G = F_o/F_{max.}$, $S = \sin\theta/\sin\theta_{max.}$). Final atomic parameters are given in Table 1 (*a*).

Crystal Growth of $[PhCN_2S_2][S_3N_3]$ (**3**).—The salt $[S_5N_5]Cl$ (0.200 g, 0.75 mmol) was placed in one bulb of a two-bulbed reaction vessel with $(PhCN_2S_2)_2$ (0.150 g, 0.41 mmol) in the other bulb. Pentane (2 × 8 cm^3) was added to each side. Inversion of the reaction vessel allowed the two solutions to mix by slow diffusion through a medium-porosity glass sinter. After 1 month the yellow solution was removed (by syringe followed by pumping) to reveal, in the $[S_5N_5]Cl$ compartment, a dirty red powder ($[S_5N_5]Cl$) with a few gold crystals of $[(PhCN_2S_2)_2Cl][S_3N_3]$ and a very few green platelets on the surface of the $[S_5N_5]Cl$. The platelets were identified by *X*-ray single-crystal analysis as $[PhCN_2S_2][S_3N_3]$.

Crystal data. $C_7H_5N_5S_5$, $M = 319.45$, triclinic, space group $P\bar{1}$, $a = 6.113(1)$, $b = 8.661(1)$, $c = 12.124(2)$ Å, $\alpha = 86.29(1)$, $\beta = 76.50(1)$, $\gamma = 70.18(1)$ °, $U = 587.12$ Å^3, $Z = 2$, $D_c = 1.807$ g cm^{-3}, $F(000) = 324$, $\mu(Mo\text{-}K_\alpha) = 0.93$ mm^{-1}, crystal size 0.04 × 0.15 × 0.40 mm, in Lindemann capillary, $T = 295$ K.

Data collection and structure determination were as for compound (**2**), except as noted: scan range 0.68° below α_1 to 0.68° above α_2; scan time 17.5—70 s, $2\theta_{max.} = 50°$; h −7 to 7, k −10 to 10, l 0 to 14, plus a partial equivalent set with h 0 to 7, k −10 to 10, l −14 to 0. 2 881 Reflections measured, 2 091 unique, 1 289 with $F > 4\sigma_c(F)$, $R_{int} = 0.019$, $R = 0.034$, $R' = 0.030$, 155 parameters, mean shift/e.s.d. = 0.002, maximum = 0.006, largest peak +0.27, largest hole −0.32 e Å^{-3}, goodness of fit 1.00, weighting scheme $w^{-1} = \sigma_c^2(F) - 1 + 14G - 5G^2 + 2S - 23GS$. Final atomic parameters are given in Table 1 (*b*).

Crystal Growth of $[PhCN_2S_2][S_3N_2]Cl$ (**4**).—The salt $[S_4N_3]Cl$ (0.100 g, 0.487 mmol) was placed in one bulb of a two-bulbed reaction vessel with $(PhCN_2S_2)_2$ (0.088 g, 0.243 mmol) in the other bulb. Acetonitrile (8 cm^3) was added to each side. Inversion of the reaction vessel allowed the solutions to mix by slow diffusion, over a period of 1 week, through a medium-porosity glass sinter. Removal of the brown solution (by syringe and pumping) revealed many orange (S_4N_4 and $[PhCN_2S_2]Cl$), black ($[PhCN_2S_2]_2Cl$), and a few gold-coloured crystals $\{[(PhCN_2S_2)_2Cl][S_3N_3]\}$ interspersed with a very small number of shiny green platelets, and a faint white haze on the glass (sulphur). A small amount of a deep red compound was collected in the cold trap and identified by its typical colour and iodine-like smell as S_4N_2. The green platelets of (**4**) were identified by *X*-ray single-crystal analysis.

Crystal data. $C_7H_5ClN_4S_5$, $M = 340.9$, monoclinic, space group $P2_1/c$, $a = 9.452(2)$, $b = 14.995(3)$, $c = 9.716(2)$ Å, $\beta = 114.07(1)$ °, $U = 1\,257.3$ Å^3, $Z = 4$, $D_c = 1.774$ g cm^{-3}. $F(000) = 688$, $\mu(Mo\text{-}K_\alpha) = 1.08$ mm^{-1}, crystal size 0.37 × 0.48 × 0.04 mm, in Lindemann capillary, $T = 295$ K.

Data collection and structure determination were as for compound (**2**), except as noted: scan range 0.51° below α_1 to 0.51° above α_2; scan time 17.5—70 s, $2\theta_{max.} = 50°$; h −11 to 11, k 0 to 17, l 0 to 11, plus a few equivalents with k, l, <0. 2 450 Reflections measured, 2 223 unique, 1 327 with $F > 4\sigma_c(F)$, $R_{int} = 0.031$, $R = 0.049$, $R' = 0.045$, 154 parameters, mean shift/e.s.d. = 0.001, maximum = 0.008, largest peak = +1.0, largest hole −0.42 e Å^{-3}, goodness of fit 1.48, weighting scheme $w^{-1} = \sigma_c^2(F) + 27 - 227G + 689G^2 - 32S + 16S^2 + 42GS$. Final atomic parameters are given in Table 1(*c*).

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

Preparation of $[PhCN_2S_2][AsF_6]$ (**5**).—The salt $[PhCN_2S_2]Cl$ (1.000 g, 3.766 mmol), $AgAsF_6$ (1.118 g, 3.766 mmol), and a Teflon-coated magnetic stirrer bar were placed in one bulb of a two-bulbed reaction vessel. Sulphur dioxide (10 cm^3) was condensed onto the mixture using an acetone–solid CO_2 bath at −78 °C and the mixture was warmed to room temperature with

Table 1. Final atomic co-ordinates (× 10^4)

(*a*) $[(PhCN_2S_2)_2Cl][S_3N_3]$

Atom	*x*	*y*	*z*
S(11)	579(1)	4 150(1)	2 842(1)
S(12)	−122(1)	3 734(1)	1 027(1)
N(11)	2 386(3)	5 364(3)	3 169(2)
N(12)	1 597(3)	4 916(3)	1 099(2)
C(11)	2 732(4)	5 648(3)	2 203(3)
C(12)	4 339(4)	6 766(3)	2 379(3)
C(13)	4 648(5)	7 115(4)	1 391(4)
C(14)	6 176(6)	8 200(5)	1 590(6)
C(15)	7 342(6)	8 886(5)	2 728(7)
C(16)	7 046(5)	8 538(4)	3 711(5)
C(17)	5 539(4)	7 481(4)	3 534(4)
S(21)	3 563(1)	−43(1)	1 150(1)
S(22)	5 110(1)	1 017(1)	2 911(1)
N(21)	2 102(3)	−1 093(3)	1 455(2)
N(22)	3 857(3)	119(3)	3 456(3)
C(21)	2 420(4)	−912(3)	2 630(3)
C(22)	1 218(4)	−1 872(3)	3 032(2)
C(23)	1 651(5)	−1 780(4)	4 242(3)
C(24)	555(5)	−2 677(5)	4 632(4)
C(25)	−970(5)	−3 672(4)	3 824(4)
C(26)	−1 411(5)	−3 789(4)	2 618(4)
C(27)	−341(4)	−2 887(4)	2 204(3)
S(31)	4 392(1)	3 538(1)	3 046(1)
S(32)	1 251(1)	1 684(1)	2 887(1)
S(33)	1 853(1)	1 850(1)	771(1)
N(31)	3 665(4)	3 063(4)	1 618(3)
N(32)	3 137(4)	2 849(4)	3 656(3)
N(33)	710(3)	1 206(3)	1 467(3)
Cl	−2 922(1)	2 050(1)	1 538(1)

(*b*) $[PhCN_2S_2][S_3N_3]$

Atom	*x*	*y*	*z*
C(1)	6 264(6)	4 343(4)	3 285(3)
C(2)	5 490(6)	5 443(4)	2 370(3)
C(3)	6 629(7)	6 574(5)	1 948(3)
C(4)	5 935(7)	7 599(5)	1 085(4)
C(5)	4 153(6)	7 501(5)	614(3)
C(6)	3 012(7)	6 377(5)	1 030(4)
C(7)	3 656(7)	5 360(5)	1 901(3)
N(1)	8 168(6)	4 373(4)	3 652(3)
N(2)	5 076(5)	3 328(4)	3 743(3)
S(1)	8 850(2)	3 108(1)	4 652(1)
S(2)	6 117(2)	2 183(1)	4 739(1)
N(3)	11 035(5)	−536(4)	3 609(3)
S(3)	8 779(2)	−571(1)	3 134(1)
N(4)	8 343(6)	457(4)	2 039(3)
S(4)	9 829(2)	1 641(1)	1 417(1)
N(5)	11 962(6)	1 639(4)	2 019(3)
S(5)	12 520(2)	684(1)	3 116(1)

(*c*) $[PhCN_2S_2][S_3N_2]Cl$

Atom	*x*	*y*	*z*
S(11)	1 613(1)	4 161(1)	6 519(1)
S(12)	3 473(1)	4 211(1)	8 592(1)
N(11)	2 250(5)	4 877(3)	5 655(5)
N(12)	4 370(5)	4 917(3)	7 995(5)
C(11)	3 611(6)	5 209(3)	6 542(5)
C(12)	4 331(5)	5 876(3)	5 890(6)
C(13)	3 639(6)	6 123(3)	4 365(6)
C(14)	4 366(7)	6 712(3)	3 748(6)
C(15)	5 755(7)	7 048(4)	4 687(7)
C(16)	6 456(7)	6 804(4)	6 239(7)
C(17)	5 720(6)	6 226(3)	6 847(7)
S(21)	−17(1)	5 247(1)	7 803(1)
S(22)	1 988(1)	5 324(1)	9 918(1)
S(23)	1 456(2)	6 854(2)	8 154(2)
N(21)	2 479(5)	6 330(3)	9 655(6)
N(22)	103(5)	6 246(3)	7 179(6)
Cl	778(2)	3 493(1)	9 211(2)

vigorous stirring. Almost immediately a white precipitate and a bright orange solution were formed. After 24 h the mixture was filtered and the insoluble white precipitate of AgCl washed with back-distilled SO_2 (3 × 10 cm^3). Removal of the solvent afforded AgCl (which darkened on exposure to light) and a bright orange solid (1.35 g, 97%); i.r. $\nu_{max.}$ at 1 549m, 1 500m, 1 395s, 1 297w, 1 202w, 1 185m (sh), 1 160m, 1 148m (sh), 1 070w, 1 030m, 1 002w, 928m, 915m, 846m, 789m (sh), 785m, 692vs, 555m, and 400vs cm^{-1} (Found: C, 22.5; H, 1.35; As, 20.0; F, 31.0; N, 7.5; S, 17.5. $C_7H_5AsF_6N_2S_2$ requires C, 22.5; H, 1.35; As, 20.0; F, 31.0; N, 7.5; S, 17.0%).

Large-scale Preparation of $[(PhCN_2S_2)_2Cl][S_3N_3]$ (**2**).—The salt $[S_5N_5]Cl$ (0.375 g, 1.41 mmol), $(PhCN_2S_2)_2$ (0.625 g, 1.73 mmol), and acetonitrile (55 cm^3) were placed together, with a Teflon-coated stirrer bar, in a round-bottomed flask (250 cm^{-3}). After 24 h of stirring at 25 °C the solution was red with a golden precipitate. The mixture was filtered, the golden solid washed with acetonitrile (3 × 10 cm^3), and the solvent removed by pumping (0.441 g, 56%); i.r. $\nu_{max.}$ at 1 596w, 1 405w (sh), 1 184w, 1 175w, 1 140m, 1 027w, 945m (br), 925w (sh), 906m, 891w (sh), 878w, 871w (sh), 813s, 770w, 720w, 693w, 682m, 675w (sh), 666m, 541m, 495w, 483w, and 470w (sh) cm^{-1} (Found: C, 31.30; H, 1.90; Cl, 7.30; N, 17.95; S, 40.05. $C_{14}H_{10}ClN_7S_7$ requires C, 31.30; H, 1.85; Cl, 6.60; N, 18.25; S, 41.75%). Mass spectroscopy (m.s.) (e.i.): *m/z* 181 ($[PhCN_2S_2]^+$, 100) and 138 ($[S_3N_3]^+$, 9.8%). D.s.c. (4 °C min^{-1}): 138—145 (weak exotherm), 145—148 °C (weak endotherm), 148—160 (strong exotherm), 160—175 (medium exotherm), and 175—250 °C (medium exotherm).

Large-scale Preparation of $[PhCN_2S_2][S_3N_3]$ (**3**).—The salt $[PhCN_2S_2][AsF_6]$ (0.114 g, 0.308 mmol) and $[NPr_4][S_3N_3]$ (0.100 g, 0.320 mmol) were placed together, with a Teflon-coated stirrer bar, in one bulb of a two-bulbed reaction vessel. On addition of acetonitrile (10 cm^3) a deep red solution and a dark green precipitate formed. After stirring for 1 d the now pale red solution was filtered off and the solvent removed by pumping to give a dirty red solid which was identified by i.r. spectroscopy as principally $[NPr_4][AsF_6]$. The crude green solid was then sublimed (70 °C, 4 × 10^{-6} Torr) and the green product collected on a cold-finger at −20 °C (0.099 g, 57%); i.r. $\nu_{max.}$ at 1 595w, 1 240w, 1 184m, 1 147m, 1 078w (br), 1 028m, 990m (br), 927w, 908m, 853m, 844w (sh), 806s, 775s, 726w, 700m, 687m, 663m, 648s, 605m, 550w, 535w, and 458w cm^{-1} (Found: C, 26.40; H, 1.50; N, 22.10; S, 50.05. $C_7H_5N_5S_5$ requires C, 26.30; H, 1.55; N, 21.95; S, 50.15%). M.s. (e.i.): *m/z* 181 ($[PhCN_2S_2]^+$, 100) and 138 (S_3N_3, 9.8%). D.s.c. (4 °C min^{-1}): 125—140 (weak endotherm) and 140—205 °C (strong broad exotherm).

Large-scale Preparation of $[PhCN_2S_2][S_3N_2]Cl$ (**4**).—The salt $[S_3N_2Cl][FeCl_4]$ (0.300 g, 0.84 mmol) and $(PhCN_2S_2)_2$ (0.300 g, 0.83 mmol) were placed together, with a Teflon-coated stirrer bar, in a one bulb of a two-bulbed reaction vessel. Acetonitrile (10 cm^3) was added and immediately a dark green

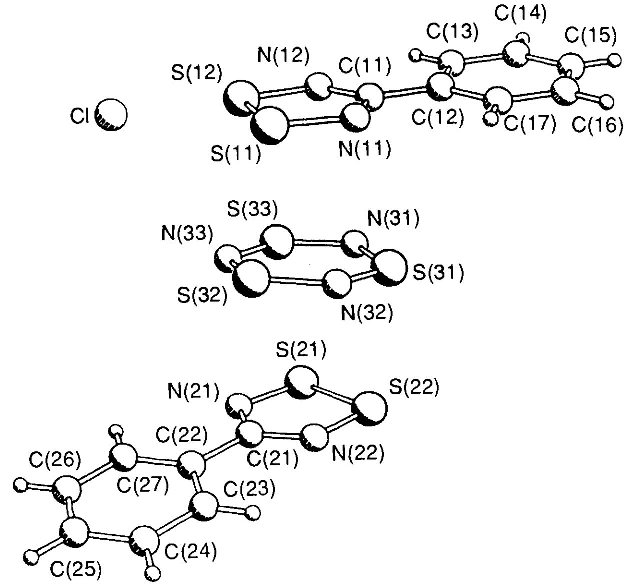


Figure 2. The structure of $[(PhCN_2S_2)_2Cl][S_3N_3]$ (**2**), showing the atom labelling of the asymmetric unit and the parallel rings

precipitate was formed. The mixture was stirred for 1 d, the brown solution filtered, and the green precipitate washed with back-distilled acetonitrile (3 × 10 cm^3). The solvent was removed by pumping to give a brown sticky tar and a crude green solid which was extracted in a closed extractor with acetonitrile for 1 d (158 mg, 56%); i.r. $\nu_{max.}$ at 1 250w, 1 167w, 1 142w, 1 025w, 987w, 941m, 910m, 862m, 818s, 810 (sh), 790m, 722w, 705s, 697s, 578w, and 538m cm^{-1} (Found: C, 24.00; H, 1.35; Cl, 11.30; N, 16.45; S, 46.40. $C_7H_5ClN_4S_5$ requires C, 24.65; H, 1.45; Cl, 10.45; N, 16.45; S, 47.00%). M.s. (e.i.): *m*/*z* 181 ($[PhCN_2S_2]^+$, 98), 149 ($[PhCN_2S]^+$, 14), 135 ($[PhCNS]^+$, 37), 124 ($[S_3N_2]^+$, 6), and 92 ($[S_2N_2]^+$, 9%). D.s.c. (4 °C min^{-1}): 138—154 (strong exotherm), 154—173 (weak exotherm), and 173—220 °C (medium exotherm).

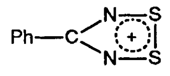
Reaction Between $[S_5N_5][AlCl_4]$ *and* $(PhCN_2S_2)_2$ *to produce* $[PhCN_2S_2][S_3N_3]$ (**3**).—The salt $[S_5N_5][AlCl_4]$ (0.165 g, 0.41 mmol) was placed in one bulb of a two bulbed reaction vessel with $(PhCN_2S_2)_2$ (0.150 g, 0.41 mmol) in the other bulb. Acetonitrile (2 × 8 cm^3) was added and the vessel inverted in a typical crystal-growth experiment. After a few minutes the solution in the dimer compartment was deep red. After 2 d the dimer compartment contained many shiny green platelets ($[PhCN_2S_2][S_3N_3]$) interspersed by a few yellow crystals (S_4N_4). The mixture was filtered, washed with back-distilled acetonitrile (2 × 5 cm^3), and the solvent removed by pumping to reveal a green microcrystalline solid, (**3**) (21 mg, 16%); i.r. $\nu_{max.}$ at 1 595w, 1 240w, 1 184m, 1 147m, 1 078w (br), 1 028m, 990m (br), 927w, 908m, 853m, 844w (sh), 806s, 775s, 726w, 700m, 687m, 663m, 648s, 605m, 550w, 535w, and 458w cm^{-1}.

Mixing Vapours of $(SN)_x$ *and* $(PhCN_2S_2)_2$ *to produce* $[PhCN_2S_2][S_3N_3]$ (**3**)—Vapours of $(SN)_x$ (*ca.* 0.042 g, 0.913 mmol at 160 °C) and $(PhCN_2S_2)_2$ (0.022 g, 0.061 mmol at 50 °C) were mixed through quartz wool under high vacuum (3 × 10^{-6} Torr) at 160 °C [see Figure 1(*b*)]. The product was collected on a cold-finger at −196 °C and resublimed at 70 °C to separate the excess of $(SN)_x$ from the green product which was identified by its i.r. spectrum as a mixture of $[PhCN_2S_2][S_3N_3]$, S_4N_4, and $(PhCN_2S_2)_2$; i.r. $\nu_{max.}$ at 1 597w[a], 1 322vw[a], 1 242w[a], 1 187m[a], 1 158w (sh)[a], 1 144m[a], 1 101w[a], 1 077w[a], 1 025m[a], 990m[a], 928s[b], 906m[a], 803s[a], 778m[c], 770s[a], 726m[a], 706s (sh)[a], 698s[b], 682m[c], 658m[a], 644m[a], 605w[a], 550s[b], 530m[a], 510w[c], and 457w[a] cm^{-1}, where [a] = $[PhCN_2S_2]$-$[S_3N_3]$, [b] = S_4N_4, and [c] = $(PhCN_2S_2)_2$.

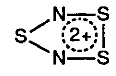
Preparation of $[PhCN_2S_2]_2Cl$ (**7**).—The dimer $(PhCN_2S_2)_2$ (0.100 g, 0.276 mmol) was ground together with $[PhCN_2S_2]Cl$ (0.1196 g, 0.552 mmol) in an agate pestle and mortar. Initially the mixture was sticky but on persistent grinding a brown powder resulted, which was heated at 156 °C for 15 min under a blanket of nitrogen to produce $[PhCN_2S_2]_2Cl$ quantitatively as indicated by the absence of characteristic i.r. peaks for both of the starting materials; i.r. $\nu_{max.}$ at 1 600w (br), 1 395s (sh), 1 260w, 1 213w, 1 177m, 1 130s, 1 070w, 1 024m, 1 000vw, 939w, 925w, 911m, 902m, 879m, 856w, 832m, 807s, 782s, 772s, 696s (sh), 689s, 676m, 667m, 662m (sh), 650m (sh), 540m, 525m, 489w, and 470s cm^{-1} (Found: C, 42.55; H, 2.60; N, 14.10; S, 33.20. $C_{14}H_{10}ClN_4S_4$ requires C, 42.25; H, 2.50; N, 14.10; S, 32.10%). M.s. (e.i.): *m*/*z* 181 ($[PhCN_2S_2]^+$, 100%). D.s.c. (4 °C min^{-1}): 135—158 (weak endotherm) and 158—187 °C (strong exotherm).

Results and Discussion

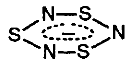
In this section, we refer to compounds containing three ring systems which are formally (*a*)—(*c*).



(*a*)

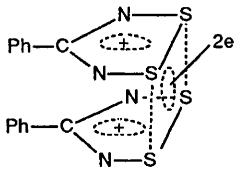


(*b*)



(*c*)

For electron-counting purposes, these are regarded as 6π in (*a*) and (*b*), and 10π in (*c*); in two compounds [(**1**) and (**4**)] there is also a four-centre two-electron interaction between the sulphur atoms of 2 (*a*) rings or (*a*) and (*b*) respectively. The structure of the dithiadiazole dimer is therefore formally as below. In



(**1**)

practice, as discussed below, the ring charges are much less than indicated above, and the four-centre interactions are weak due to loss of charge to the strongly withdrawing (high electronegativity) ring nitrogen atoms of (*a*) and (*b*).

We first consider the crystal structures of the three new compounds, then aspects of bonding. After a discussion of mechanistic aspects, we comment on the various preparations.

The Crystal Structures of $[(PhCN_2S_2)_2Cl][S_3N_3]$, $[PhCN_2S_2][S_3N_3]$, *and* $[PhCN_2S_2][S_3N_2]Cl$.—(*a*) $[(PhCN_2S_2)_2Cl]$-$[S_3N_3]$. Crystals of a suitable size for *X*-ray structure determination were grown by allowing a saturated solution of $(PhCN_2S_2)_2$, in acetonitrile, to diffuse slowly into a very weak but saturated solution of $[S_5N_5]Cl$ above excess of $[S_5N_5]Cl$. Slow diffusion greatly reduced the number of nucleation sites, hence the formation of a few, large (up to 10 mm long), well faceted golden crystals. These were surprisingly air stable and could be isolated and mounted in an open atmosphere with negligible decomposition. The asymmetric unit (Figure 2) shows the almost planar S_3N_3 ring sandwiched between two CN_2S_2 rings in a parallel arrangement. There are significant S · · · S interactions between the CN_2S_2 and S_3N_3 rings, the

Table 2. Bond lengths (Å) and angles (°) within $[(PhCN_2S_2)_2Cl][S_3N_3]$ molecules

S(11)–S(12)	2.034(1)	S(11)–N(11)	1.597(3)
S(12)–N(12)	1.611(3)	N(11)–C(11)	1.359(5)
N(12)–C(11)	1.329(3)	C(11)–C(12)	1.469(4)
C(12)–C(13)	1.391(7)	C(12)–C(17)	1.389(5)
C(13)–C(14)	1.396(6)	C(14)–C(15)	1.362(8)
C(15)–C(16)	1.380(11)	C(16)–C(17)	1.377(5)
S(21)–S(22)	2.047(1)	S(21)–N(21)	1.607(3)
S(22)–N(22)	1.606(3)	N(21)–C(21)	1.340(5)
N(22)–C(21)	1.344(3)	C(21)–C(22)	1.482(5)
C(22)–C(23)	1.384(5)	C(22)–C(27)	1.399(4)
C(23)–C(24)	1.380(7)	C(24)–C(25)	1.369(5)
C(25)–C(26)	1.375(7)	C(26)–C(27)	1.384(6)
S(31)–N(31)	1.587(4)	S(31)–N(32)	1.597(4)
S(32)–N(32)	1.615(3)	S(32)–N(33)	1.590(4)
S(33)–N(31)	1.603(3)	S(33)–N(33)	1.593(4)
S(21′)–Cl	3.082(2)	S(22′)–Cl	2.897(2)
S(11)–Cl	2.964(2)	S(12)–Cl	2.903(2)
S(31)–S(22)	3.002(2)	S(32)–S(11)	2.929(2)
S(33)–S(12)	3.263(2)	S(33)–S(21)	3.032(2)
S(12)–S(11)–N(11)	95.7(1)	S(11)–S(12)–N(12)	94.6(1)
S(11)–N(11)–C(11)	114.7(2)	S(12)–N(12)–C(11)	115.6(3)
N(11)–C(11)–N(12)	119.4(3)	N(11)–C(11)–C(12)	120.2(2)
N(12)–C(11)–C(12)	120.4(3)	C(11)–C(12)–C(13)	119.9(3)
C(11)–C(12)–C(13)	119.8(4)	C(13)–C(12)–C(17)	120.2(3)
C(12)–C(13)–C(14)	118.6(4)	C(13)–C(14)–C(15)	120.4(7)
C(14)–C(15)–C(16)	121.3(5)	C(15)–C(16)–C(17)	119.2(4)
C(12)–C(17)–C(16)	120.3(5)	S(22)–S(21)–N(21)	94.8(1)
S(21)–S(22)–N(22)	95.1(1)	S(21)–N(21)–C(21)	115.1(2)
S(22)–N(22)–C(21)	114.8(3)	N(21)–C(21)–N(22)	120.1(3)
N(21)–C(21)–C(22)	120.4(2)	N(22)–C(21)–C(22)	119.4(3)
C(21)–C(22)–C(23)	119.5(2)	C(21)–C(22)–C(27)	121.1(3)
C(23)–C(22)–C(27)	119.4(3)	C(22)–C(23)–C(24)	120.4(3)
C(23)–C(24)–C(25)	120.3(4)	C(24)–C(25)–C(26)	119.9(5)
C(25)–C(26)–C(27)	121.0(3)	C(22)–C(27)–C(26)	119.0(4)
N(31)–S(31)–N(32)	116.2(2)	N(32)–S(32)–N(33)	116.1(2)
N(31)–S(33)–N(33)	114.8(2)	S(31)–N(31)–S(33)	124.9(3)
S(31)–N(32)–S(32)	122.9(2)	S(32)–N(33)–S(33)	124.9(2)

S(21′) and S(22′) are generated from S(21) and S(22) by the operation $-1 + x, y, z$.

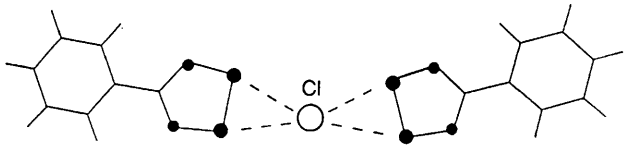


Figure 3. The new planar cation, $[PhCN_2S_2]_2Cl^+$, in (**2**)

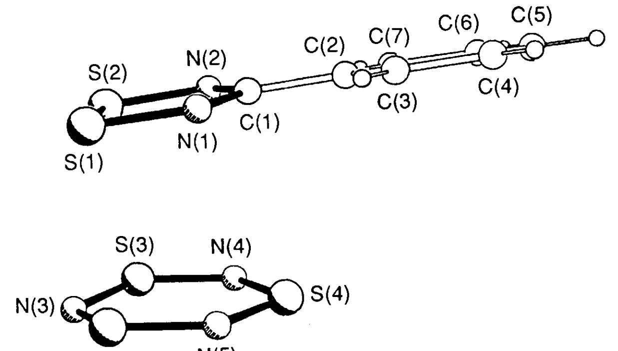


Figure 4. The structure of $[PhCN_2S_2][S_3N_3]$ (**3**), showing the atom labelling of the asymmetric unit

Table 3. Bond lengths (Å) and angles (°) within $[PhCN_2S_2][S_3N_3]$ molecules

C(1)–C(2)	1.471(5)	C(1)–N(1)	1.349(6)
C(1)–N(2)	1.338(5)	C(2)–C(3)	1.392(6)
C(2)–C(7)	1.394(7)	C(3)–C(4)	1.376(6)
C(4)–C(5)	1.370(7)	C(5)–C(6)	1.386(7)
C(6)–C(7)	1.373(6)	N(1)–S(1)	1.611(3)
N(2)–S(2)	1.619(3)	S(1)–S(2)	2.064(2)
N(3)–S(3)	1.623(4)	N(3)–S(5)	1.616(4)
S(3)–N(4)	1.574(4)	N(4)–S(4)	1.630(4)
S(4)–N(5)	1.636(4)	N(5)–S(5)	1.564(4)
S(1)–S(5)	2.876(3)	S(2)–S(3)	2.935(3)
C(2)–C(1)–N(1)	119.4(4)	C(2)–C(1)–N(2)	119.9(4)
N(1)–C(1)–N(2)	120.8(3)	C(1)–C(2)–C(3)	119.7(4)
C(1)–C(2)–C(7)	121.3(4)	C(3)–C(2)–C(7)	119.0(4)
C(2)–C(3)–C(4)	120.2(4)	C(3)–C(4)–C(5)	120.7(4)
C(4)–C(5)–C(6)	119.4(4)	C(5)–C(6)–C(7)	120.7(5)
C(2)–C(7)–C(6)	119.9(4)	C(1)–N(1)–S(1)	114.8(3)
C(1)–N(2)–S(2)	114.8(3)	N(1)–S(1)–S(2)	94.9(2)
N(2)–S(2)–S(1)	94.8(1)	S(3)–N(3)–S(5)	122.6(2)
N(3)–S(3)–N(4)	116.1(2)	S(3)–N(4)–S(4)	125.5(3)
N(4)–S(4)–N(5)	113.4(2)	S(4)–N(5)–S(5)	125.2(3)
N(3)–S(5)–N(5)	116.7(2)		

mean bond length (3.056 Å) being close to that in $(PhCN_2S_2)_2$ [3.109(5) Å]. A list of the important bond lengths and angles is given in Table 2.

Figure 3 shows the new planar cation, $[PhCN_2S_2]_2Cl^+$, which is slightly bent (within the plane) with the chloride ion weakly bonded to the four sulphurs in the two CN_2S_2 rings; the mean S–Cl distance [2.962(2) Å] is slightly longer than in $[PhCN_2S_2]Cl$ [2.906(5) Å][17] due to the chloride being four-co-ordinate in (**2**) compared with two-co-ordinate in $[PhCN_2S_2]Cl$.

Bond lengths and angles in the S_3N_3 ring are comparable,[18] within experimental error, to those in the known structure of $[NBu^t_4][S_3N_3]$, and those for the CN_2S_2 ring are discussed later.

(*b*) $[PhCN_2S_2][S_3N_3]$. Small green platelets of $[PhCN_2S_2][S_3N_3]$, which were suitable for *X*-ray structure analysis, were grown from pentane, as described in (*a*) for compound (**2**). Again the crystals were surprisingly air stable, only tarnishing after many hours in an open atmosphere.

The asymmetric unit (Figure 4) shows the S_3N_3 ring directly below the CN_2S_2 ring, the two planar halves being almost parallel at an angle of 6.8° to one another. Again there is significant bonding between the sulphurs in the CN_2S_2 ring and S(5) and S(3) in the S_3N_3 ring, the mean S $\cdots$ S bond length being 2.906(3) Å [*cf.* 3.109(5) Å in $(PhCN_2S_2)_2$].[4] A list of the important bond lengths and angles is given in Table 3. As in compound (**2**) the bond lengths and angles in the S_3N_3 ring are comparable, within experimental error, to those in the known structure of $[NBu^t_4][S_3N_3]$; those for the CN_2S_2 ring are discussed later.

(*c*) $[PhCN_2S_2][S_3N_2]Cl$. In a similar experiment to (*a*), single crystals of $[PhCN_2S_2][S_3N_2]Cl$ were grown by allowing a solution of $(PhCN_2S_2)_2$ in acetonitrile to diffuse slowly into a saturated solution of $[S_4N_3]Cl$ over excess of $[S_4N_3]Cl$; the chloride is virtually insoluble in acetonitrile. The small green platelets were fairly stable to moisture, only tarnishing after 15 min in a droplet of water.

The asymmetric unit (Figure 5) shows the CN_2S_2 ring bonded to the S_3N_2 ring through the disulphide sulphurs in a *cis* arrangement, the rings being inclined at 26.2° to each other. The chloride ion is weakly bonded to all four disulphide sulphurs,

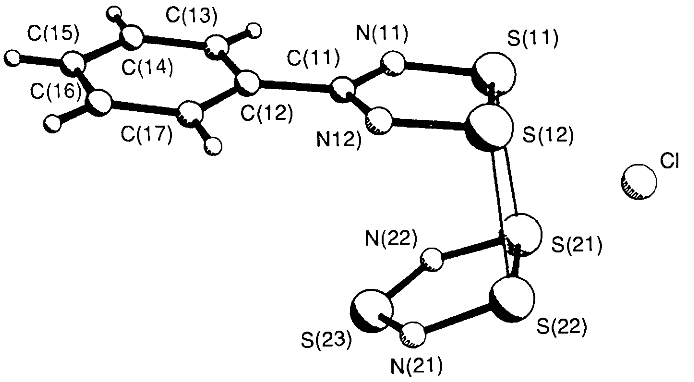


Figure 5. The structure of $[PhCN_2S_2][S_3N_2]Cl$ (4), showing the atom labelling of the asymmetric unit

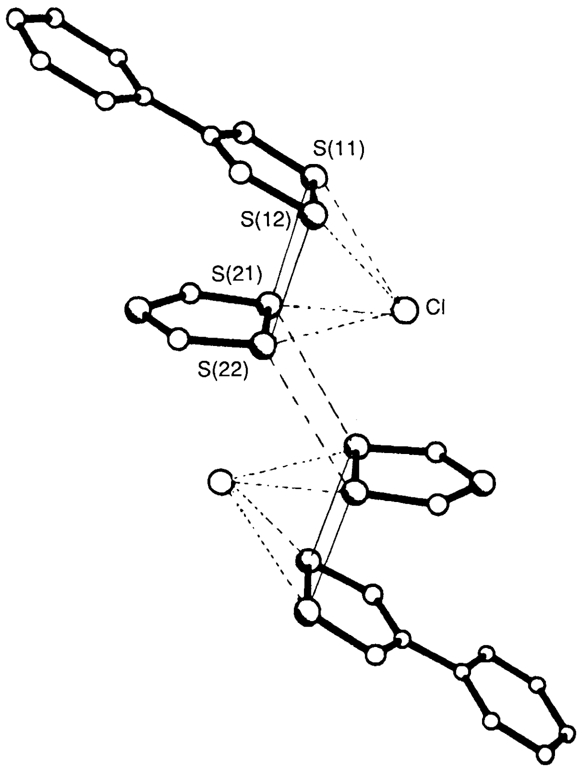


Figure 6. The weaker secondary interactions between two adjacent $[PhCN_2S_2][S_3N_2]Cl$ molecules

the average S ··· Cl distance being 3.024(3) Å. Figure 6 shows the weaker secondary interactions between two adjacent $[PhCN_2S_2][S_3N_2]Cl$ molecules, the mean S ··· S distance being 3.522(2) Å compared with the van der Waals diameter[19] of 4.0 Å perpendicular to the S ··· S bond. The sulphur bonding between the CN_2S_2 and the S_3N_2 rings is, however, much more significant, the mean S ··· S bond length being 2.838(2) compared with 3.109(5) Å in $(PhCN_2S_2)_2$. Table 4 lists the most important bond lengths and angles.

Bond lengths and angles in the S_3N_2 ring are comparable, within experimental error, to those in $(S_3N_2Cl)_2$,[20] except for the S–S bond which is slightly shorter in $[PhCN_2S_2][S_3N_2]Cl$ [$d_{S\cdots S}$ = 2.152(2) Å] than in $(S_3N_2Cl)_2$ [$d_{S\cdots S}$ = 2.131(2) Å].

The CN_2S_2 *Rings and the Electronic Structure.*—The S–S bond lengths in the CN_2S_2 rings are summarised in Table 5.

Table 4. Bond lengths (Å) and angles (°) within $[PhCN_2S_2][S_3N_2]Cl$ molecules

S(11)–S(12)	2.055(2)	S(11)–N(11)	1.618(5)
S(12)–N(12)	1.613(5)	N(11)–C(11)	1.339(6)
N(12)–C(11)	1.340(6)	C(11)–C(12)	1.490(8)
C(12)–C(13)	1.369(7)	C(12)–C(17)	1.385(7)
C(13)–C(14)	1.399(9)	C(14)–C(15)	1.373(8)
C(15)–C(16)	1.391(8)	C(16)–C(17)	1.388(10)
S(21)–S(22)	2.152(2)	S(21)–N(22)	1.632(5)
S(22)–N(21)	1.632(5)	S(23)–N(21)	1.570(5)
S(23)–N(22)	1.556(5)	S(11)–S(21)	2.864(2)
S(12)–S(22)	2.812(2)	S(21′)–S(22)	3.522(2)
S(22′)–S(21)	3.522(2)	S(11)–Cl	3.134(3)
S(12)–Cl	3.100(3)	S(21)–Cl	2.907(3)
S(22)–Cl	2.954(3)		

S(12)–S(11)–N(11)	95.1(2)	S(11)–S(12)–N(12)	94.6(1)
S(11)–N(11)–C(11)	114.5(4)	S(12)–N(12)–C(11)	115.1(3)
N(11)–C(11)–N(12)	120.6(5)	N(11)–C(11)–C(12)	120.1(4)
N(12)–C(11)–C(12)	119.2(4)	C(11)–C(12)–C(13)	120.3(4)
C(11)–C(12)–C(17)	118.7(5)	C(13)–C(12)–C(17)	121.0(6)
C(12)–C(13)–C(14)	119.7(5)	C(13)–C(14)–C(15)	119.5(5)
C(14)–C(15)–C(16)	120.9(6)	C(15)–C(16)–C(17)	119.2(5)
C(12)–C(17)–C(16)	119.7(5)	S(22)–S(21)–N(22)	96.6(2)
S(21)–S(22)–N(21)	96.8(2)	N(21)–S(23)–N(22)	108.2(3)
S(22)–N(21)–S(23)	118.9(3)	S(21)–N(22)–S(23)	119.4(3)

S(21′) and S(22′) are generated from S(21) and S(22) by the operation $-x, 1-y, 2-z$.

Table 5. Summary of the S–S bond lengths in compounds (1)—(6)

Compound	Mean S–S bond length (Å) in CN_2S_2 ring
(1)[a] $(PhCN_2S)_2$	2.089(5)
(3)[b] $[PhCN_2S_2][S_3N_3]$	2.064(2)
(4)[b] $[PhCN_2S_2][S_3N_2]Cl$	2.055(2)
(2)[b] $[(PhCN_2S_2)_2Cl][S_3N_3]$	2.040(1)
(5)[c] $[PhCN_2S_2][AsF_6]$	2.023(1)
(6)[d] $[PhCN_2S_2]Cl$	1.990(5)

[a] Ref. 4. [b] This work. [c] Ref. 22. [d] Ref. 17.

These can be rationalised on the basis that (*i*), in $[PhCN_2S_2]Cl$,[17] covalent interaction between $PhCN_2S_2{}^+$ and Cl^- strengthens the S–S bond as in other dithiolium halides;[21] (*ii*) in the $[PhCN_2S_2][AsF_6]$ salt[22] the $PhCN_2S_2{}^+$ cation is essentially ionic with negligible covalent cation-anion interaction, and (*iii*) in the other compounds further electron density on the $PhCN_2S_2{}^+$ ring causes lengthening of the S–S bond [the singly occupied molecular orbital (s.o.m.o.) in $PhCN_2S_2{}^•$ is antibonding[23] with respect to S–S, see Figure 7]; hence the difference in S–S bond lengths, in 6π $[PhCN_2S_2][AsF_6]$ [d_{S-S} = 2.023(2) Å] and the >6π monomer in $(PhCN_2S_2)_2$ [d_{S-S} = 2.089(5) Å], is directly related to the electron density of the s.o.m.o. in the $PhCN_2S_2$ (some of the extra electron density in the dimer will, of course, be occupied in the weak S ··· S bonds between the rings).

(*a*) $[PhCN_2S_2][S_3N_3]$, (3). The S–S distance in compound (3) [2.064(2) Å] is slightly closer to that in >6π (1) than in 6π (5) (Table 5) suggesting appreciable electron donation from the S_3N_3 anion into the CN_2S_2 cation. One might expect compound (3) to be predominantly ionic in view of the relative instability of the $S_3N_3{}^•$ radical which is only known as a short-lived species in solution[10] or vapour,[24] but theoretical calculations (see later) indicate that in the gas phase $[PhCN_2S_2][S_3N_3]$ would exist as two interacting radicals with virtually no charge transfer from $S_3N_3{}^•$ to $PhCN_2S_2{}^•$ [*cf.* $(PhCN_2S_2)_2$]. However, crystal-field effects[25] and inadequacies

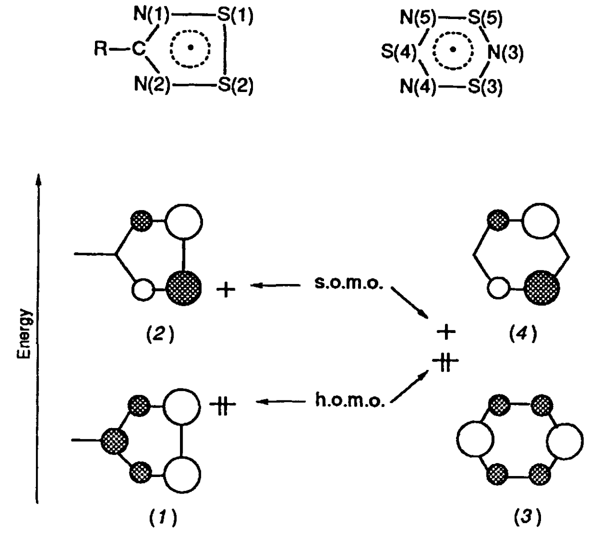


Figure 7. The relevant frontier orbitals for the RCN_2S_2 and S_3N_3 fragments

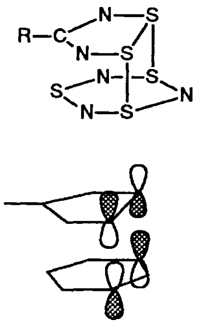


Figure 8. The favourable s.o.m.o. (2)—(4) interactions in $[PhCN_2S_2][S_3N_3]$

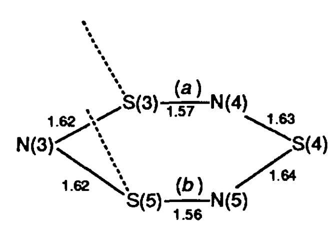


Figure 9. The S_3N_3 ring in compound (3) showing the two shortest S–N bonds (Å), (a) and (b)

of the *ab initio* basis set could well be responsible for the discrepancy.

(*b*) $[(PhCN_2S_2)_2Cl][S_3N_3]$, (2). The mean S–S bond length of 2.040(1) Å in compound (2) is shorter than in $[PhCN_2S_2][S_3N_3]$ and closer to that of the cation in compound (5). As for $[PhCN_2S_2][S_3N_3]$ the $S_3N_3^-$ ring donates electron density into the $CN_2S_2^+$ ring causing a lengthening of the S–S bond. However, the chloride ion will have a counteracting effect resulting in this shorter distance compared with compound (3).

(*c*) $[PhCN_2S_2][S_3N_2]Cl$, (4). The S–S distance in compound (4) is intermediate between compounds (1) and (5). The neutral S_3N_2 ring has been shown[26] by a Hückel m.o. scheme and Hund's rules to have a triplet ground state, thus being unstable; there is as yet very little evidence for its existence. In contrast the radical cation $S_3N_2^{\cdot+}$ is well known, existing almost entirely as the dimer $[(S_3N_2)_2]^{2+}$ in salts with various anions.[27–29]

The S–S bond length in $S_3N_2^{\cdot+}$ (like $PhCN_2S_2^{\cdot}$) is sensitive to removal of charge since the s.o.m.o. is antibonding[27] with respect to the S–S bond. Therefore, the slight lengthening of the S–S bond in the S_3N_2 ring of $[PhCN_2S_2][S_3N_2]Cl$ [d_{S-S} = 2.152(2) Å] compared with that in $(S_3N_2Cl)_2$ [d_{S-S} = 2.131(2) Å][30] can be regarded as due to slight electron donation from $PhCN_2S_2$; this donation, as well as the covalent interaction with the chloride ion, gives rise to the intermediate S–S distance in the CN_2S_2 ring (see Table 5). Thus $[PhCN_2S_2][S_3N_2]Cl$ appears to have $[PhCN_2S_2^{\cdot}][S_3N_2^{\cdot+}]Cl^-$ as its major canonical structure.

Extended Hückel and Ab Initio *M.O. Calculations on* $[PhCN_2S_2][S_3N_3]$.—Compound (3) can be considered as a pair of ions $[PhCN_2S_2][S_3N_3]^-$, a pair of radicals $[PhCN_2S_2]^{\cdot}[S_3N_3]^{\cdot}$ (singlet or triplet), or as an intermediate structure. In an attempt to gain some insight into the electronic structure of (3) we have carried out a series of theoretical calculations ranging from extended Hückel[31] to *ab initio*.[32]

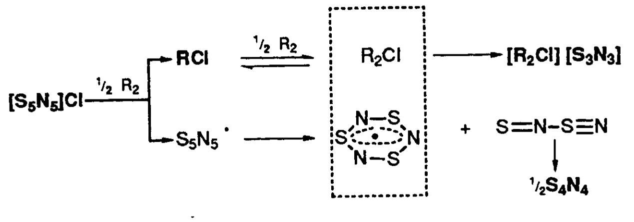
The relevant frontier orbitals for the RCN_2S_2 and S_3N_3 fragments are depicted in Figure 7 with orbital occupancy shown for $[RCN_2S_2]^{\cdot}[S_3N_3]^{\cdot}$. The ordering of the orbitals is taken from open-shell calculations (*i.e.* for radicals). Calculations for the ions show a similar ordering in the case of $[RCN_2S_2]^+$, but for $[S_3N_3]^-$ the orbitals (*3*) and (*4*) change to a degenerate pair. Conversion from radicals into ions requires transfer of the CN_2S_2 unpaired electron, at (*2*), to orbital (*4*) of S_3N_3. The symmetries of these frontier orbitals seem to favour s.o.m.o. (*2*)—(*4*) interaction as shown in Figure 8. The interaction between these two rings is now analysed by the extended-Hückel fragment m.o. analysis method.[33,34]

This orbital interaction [(*2*)—(*4*)] causes an increase in two [S(3)–N(4) and S(5)–N(5)] overlap populations in the S_3N_3 portion of compound (3). In $[S_3N_3]^{\cdot}$ all S–N overlap populations are 0.72 but in (3) they increase to 0.84 at S(3)–N(4) and S(5)–N(5) due to a decrease in antibonding character caused by the interaction depicted in Figure 9. By this interaction electron density is removed from the s.o.m.o. of (*4*), antibonding between S(3)–N(4) and S(5)–N(5), which is reflected in shorter bond lengths [(*a*) and (*b*)] (Figure 9). The other overlap populations in the S_3N_3 ring are not affected by the secondary interactions with RCN_2S_2.

S $\cdots$ S overlap populations between the two rings (calculated to be 0.17) are much smaller than the S–S overlap population (0.91) within RCN_2S_2. The N $\cdots$ N secondary interaction between the two rings is again small (overlap population 0.02) though not negligible.

Rationalisation of the bond-length variations within the S_3N_3 fragment in compound (1) was provided by *ab initio* calculations (using a 3—21G* basis set and assuming D_{3h} symmetry). The SN bond lengths in isolated $[S_3N_3]^{\cdot}$ and $[S_3N_3]^-$ are optimised to 1.626 and 1.628 Å (total energies −1 349.219 and −1 349.264 a.u. respectively) showing that only the SN bond lengths S(3)–N(4) and S(5)–N(5) change significantly (their constituent atoms are involved in interaction with RCN_2S_2).

Ab initio calculations (STO-3G basis set) were also used to calculate the total energy of compound (3). The calculations were performed assuming two possible spin states of (3); one in which a singlet state was considered, ^{1}(3) which schematically corresponds to an interaction of $[PhCN_2S_2]^+$ (6π system) with $[S_3N_3]^-$ (10π system), and another in a triplet ^{3}(3) state (corresponding to $[PhCN_2S_2]^{\cdot}$ and $[S_3N_3]^{\cdot}$). The total energy of the two different spin states, ^{1}(3) and ^{3}(3), was calculated to be 2 272.114 and −2 272.176 a.u., respectively, indicating that the triplet state is about 38 kcal mol^{-1} more stable than the singlet state. The sums of the atomic net charges in the 'ionic' case, *i.e. formally* $[RCN_2S_2]^+$ and $[S_3N_3]^-$, are +0.14 and −0.14 respectively, which shows that only a very small charge transfer takes place.



Scheme 1. Proposed mechanism for the formation of $[(PhCN_2S_2)_2Cl][S_3N_3]$, produced by the reaction between $[S_5N_5]Cl$ and $(PhCNSSN)_2$ (R_2) in MeCN

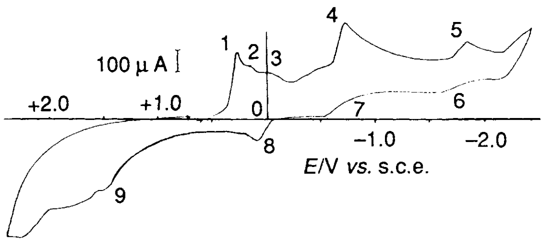
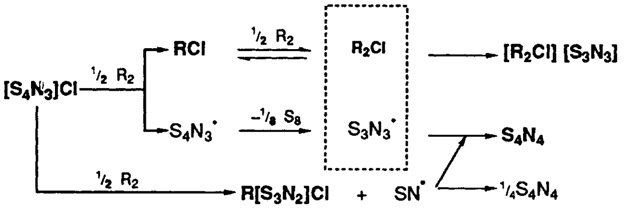


Figure 10. A typical cyclic voltammogram for $[S_4N_3][BF_4]$ (10^{-3} mol dm^{-3}) in $[NBu_4][BF_4]$ (0.1 mol dm^{-3})–MeCN; temperature +20 °C, potential sweep rate 300 mV s^{-1}



Scheme 2. Proposed mechanism for the formation of the products produced by the reaction between $[S_4N_3]Cl$ and $(PhCNSSN)_2$ (R_2) in MeCN

The 38 kcal mol^{-1} difference in energy between the two spin states indicates that, as an isolated pair of rings, compound (**3**) can be regarded as being a diradical and not an ionic system; in fact the atomic net charges on the RCN_2S_2 and S_3N_3 fragments were found to be 0.003 and −0.003 respectively for each fragment in ^{3}(**3**). Thus the two unpaired electrons in ^{3}(**3**) are located with close to one electron on each ring. For the CN_2S_2 ring the main spin populations are as follows: N, 0.62 (on each); S, 0.10 (on each); and C, −0.54. For the S_3N_3 fragment (Figure 9) the spin populations are: N(3) ≈ 0.00 (on each); N(4), N(5), 0.37; S(4), 0.27. Thus the two unpaired electrons are mainly located on nitrogen atoms placed above one another and are 3.1 Å apart. (The van der Waals radius of nitrogen is ≈ 1.5 Å.)[35]

One weakness of these calculations is that they neglect crystal-field effects; the Madelung field due to an ionic lattice might tend to stabilise the ionic form relative to the neutral form. In this context, it is instructive to remember that the diatomic molecule NaCl[25] has considerable covalent character, whereas NaCl solid is essentially ionic. Crystal-field effects may result in a significant shift in the relative energies of the orbitals of the constituent rings, and so the degree of electron transfer obtained from calculations on an isolated pair may to a certain extent be misleading. However, the theoretical calculations do provide us with some valuable information concerning the bonding and structure of the present compounds.

Mechanism of Formation.—(*a*) $[(PhCN_2S_2)_2Cl][S_3N_3]$. The trithiatriazinide ring system is normally prepared[36] from a quaternary ammonium azide and S_4N_4 in ethanol. Cyclic voltammetry has provided valuable evidence as to the mechanism of formation of the S_3N_3 ring (from $S_5N_5{}^+$) in this new route. Previous cyclic voltammetry studies[10] on $[S_5N_5]^+$ salts showed that the $[S_5N_5]^+$ ring is easily reduced to the $S_5N_5{}^{\bullet}$ radical which, being unstable, cleaves to form two neutral species thought to be S_2N_2 (linear) and $S_3N_3{}^{\bullet}$(cyclic); the latter is seen as a reduction peak producing $[S_3N_3]^-$. Fritz *et al.*[37] have also reported the reversible reduction of $S_3N_3{}^{\bullet}$(cyclic) in their cyclic voltammetry study of $[N(PPh_3)_2][S_3N_3]$ in CH_2Cl_2.

This information, and the fact that S_4N_4, $[PhCN_2S_2]Cl$, and $[PhCN_2S_2]_2Cl$ are also produced as side products in the formation of $[(PhCN_2S_2)_2Cl][S_3N_3]$, are evidence for the possible mechanism shown in Scheme 1 (the bold figures indicate products positively identified).

The salt $[S_5N_5]Cl$ is initially reduced by $(PhCN_2S_2)_2$ to produce the $S_5N_5{}^{\bullet}$ radical and $[PhCN_2S_2]Cl$ (which has been identified in the crystal-growth experiment). The $S_5N_5{}^{\bullet}$ radical then cleaves, as shown by cyclic voltammetry, to produce the $S_3N_3{}^{\bullet}$ cyclic radical and presumably the highly unstable linear S_2N_2 which dimerises to produce S_4N_4, another product identified in the crystal-growth experiment. Finally the cyclic $S_3N_3{}^{\bullet}$ radical reacts with the odd-electron species $[PhCN_2S_2]_2Cl$, to produce $[(PhCN_2S_2)_2Cl][S_3N_3]$.

(*b*) $[PhCN_2S_2][S_3N_3]$. Both $[S_5N_5]Cl$ and $(PhCN_2S_2)_2$ are practically insoluble in pentane such that little reaction occurred (even after 1 month) and hence no other compounds, except $[PhCN_2S_2][S_3N_3]$ and $[(PhCN_2S_2)_2Cl][S_3N_3]$, were identified from the reaction. From the crystals that could be seen, we estimated that $[(PhCN_2S_2)_2Cl][S_3N_3]$ was the major product with small amounts of crystalline $[PhCN_2S_2][S_3N_3]$ also present, presumably formed from $(PhCN_2S_2)_2$ and intermediate $S_3N_3{}^{\bullet}$.

The salt $[(PhCN_2S_2)_2Cl][S_3N_3]$ (**2**) is produced from the reaction between $[S_5N_5]Cl$ and $(PhCN_2S_2)_2$ in both acetonitrile and pentane, whereas $[PhCN_2S_2][S_3N_3]$ (**3**) was produced only in pentane. Although the solubilities of both (**2**) and (**3**) are not known, it is obvious from the lack of colour that both are virtually insoluble in pentane, whereas in acetonitrile a dark red colour was observed. One may assume, therefore, that it is the solubility which plays a major role in deciding which of compounds (**2**) and (**3**) is (or are) produced.

(*c*) $[PhCN_2S_2][S_3N_2]Cl$. The salt $[PhCN_2S_2][S_3N_2]Cl$ was a minor product in the reaction, being produced in an estimated yield of less than 5%, along with $[(PhCN_2S_2)_2Cl][S_3N_3]$, S_8, $[PhCN_2S_2]Cl$, $[PhCN_2S_2]_2Cl$, S_4N_4, and S_4N_2. Such a wide range of products is very likely due to reactions of highly reactive radicals produced from the reduction of $[S_4N_3]^+$.

Cyclic voltammetric studies in acetonitrile, carried out in our laboratory, on the soluble $[S_4N_3][BF_4]$[14] (Figure 10) show the non-reversible reduction of the $[S_4N_3]^+$ cation (peak 1) to the $S_4N_3{}^{\bullet}$ radical. This splits mainly into $S_3N_3{}^{\bullet}$(cyclic) (peak 3), presumably with the formation of sulphur. Peaks 4, 7, and 8 have been assigned to the reversible reduction of S_4N_4 and the oxidation of $[S_3N_3]^-$ respectively. The other smaller peaks have not been unambiguously assigned, although one may speculate that they may correspond to other S/N fragments produced from cleavage of the $S_4N_3{}^{\bullet}$ ring.

From the cyclic voltammetry data and the products positively identified in the crystal-growth reaction (compounds in bold type), we suggest Scheme 2 as a summary of the reactions. Initially $[S_4N_3]Cl$ is reduced by $(PhCN_2S_2)_2$ to produce the $S_4N_3{}^{\bullet}$ radical and $[PhCN_2S_2][S_2N_2]Cl$. Cyclic voltammetry showed that this radical is unstable, cleaving to produce mainly the $S_3N_3{}^{\bullet}$ radical {which reacts further to produce $[(PhCN_2S_2)_2Cl][S_3N_3]$ and S_4N_4} and sulphur (clearly visible on the walls of the reaction vessel). The sulphur was identified by Raman spectroscopy. The salt $[(PhCN_2S_2)_2Cl][S_3N_3]$ could be formed (*i*) from $(PhCN_2S_2)_2$ and S_4N_3Cl with elimination of

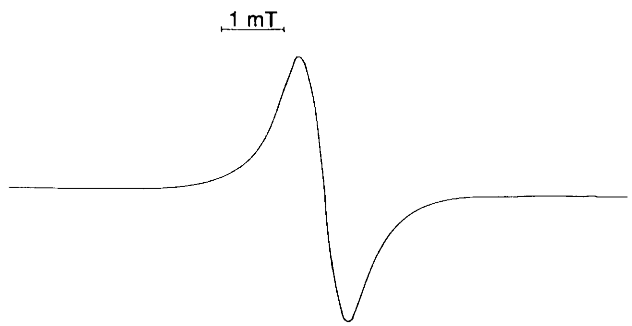


Figure 11. The e.s.r. spectrum of crystalline $[\mathrm{PhCN_2S_2}]_2\mathrm{Cl}$

$\mathrm{SN}^{\bullet}$ or (*ii*) less likely from $[\mathrm{PhCN_2S_2}]\mathrm{Cl}$ and an unobserved intermediate $\mathrm{S_3N_2}$. Reductions of $[\mathrm{S_4N_3}]\mathrm{Cl}$[38] and other S/N/Cl[39] species to produce $\mathrm{S_4N_2}$ have also been described but without mechanistic interpretation.

Large-scale Preparations.—(*a*) $[(\mathrm{PhCN_2S_2})_2\mathrm{Cl}][\mathrm{S_3N_3}]$. This compound was produced by the reaction (1:1.2) of $[\mathrm{S_5N_5}]\mathrm{Cl}$ with excess of $(\mathrm{PhCN_2S_2})_2$ in acetonitrile as a golden microcrystalline solid sparingly soluble in acetonitrile. The volume of solvent used in the reaction was very important as (*i*) the use of too much reduced the yield and (*ii*) the use of too little allowed $\mathrm{S_4N_4}$ (which could not be separated from the product) to crystallise out. The slight excess of $(\mathrm{PhCN_2S_2})_2$ was needed to ensure that no unreacted $[\mathrm{S_5N_5}]\mathrm{Cl}$ remained (which like $\mathrm{S_4N_4}$, was virtually impossible to separate from the final product).

(*b*) $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$. The salt $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$ is relatively insoluble in acetonitrile and was therefore easily prepared by precipitation from the stoicheiometric metathesis of $[\mathrm{PhCN_2S_2}][\mathrm{AsF_6}]$ and $[\mathrm{NPr_4}][\mathrm{S_3N_3}]$; the other product, $[\mathrm{NPr_4}][\mathrm{AsF_6}]$, is readily soluble in acetonitrile. After washing with acetonitrile, purification was completed by high-vacuum sublimation (*ca.* 10^{-6} Torr). The grey residue, $[\mathrm{NPr_4}][\mathrm{AsF_6}]$, was involatile.

The salt $[\mathrm{PhCN_2S_2}][\mathrm{AsF_6}]$ has previously been prepared[22] from the reaction between $\mathrm{PhC(NSN)_2CPh}$ with $\mathrm{AgAsF_6}$ in liquid $\mathrm{SO_2}$, and its *X*-ray crystal structure was determined. This salt is more conveniently prepared by simple stoicheiometric metathesis of $[\mathrm{PhCN_2S_2}]\mathrm{Cl}$ with $\mathrm{AgAsF_6}$ in liquid $\mathrm{SO_2}$ to produce pure orange crystalline $[\mathrm{PhCN_2S_2}][\mathrm{AsF_6}]$ in quantitative yield.

(*c*) $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_2}]\mathrm{Cl}$. Previous reports[20,40] have shown that the $[\mathrm{S_3N_2Cl}]^+$ ion is easily reduced to $\mathrm{S_3N_2Cl}$. Consequently when $[\mathrm{S_3N_2Cl}][\mathrm{FeCl_4}]$ was reduced by an equimolar quantity of $(\mathrm{PhCN_2S_2})_2$ in acetonitrile green microcrystalline $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_2}]\mathrm{Cl}$ was produced as shown in equation (1).

$$(\mathrm{PhCN_2S_2})_2 + [\mathrm{S_3N_2Cl}][\mathrm{FeCl_4}] \longrightarrow [\mathrm{PhCN_2S_2}][\mathrm{FeCl_4}] + [\mathrm{PhCN_2S_2}][\mathrm{S_3N_2}]\mathrm{Cl} \quad (1)$$

Reaction Between $[\mathrm{S_5N_5}][\mathrm{AlCl_4}]$ *and* $(\mathrm{PhCN_2S_2})_2$ *to produce* $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$ (3).—In an attempt to produce crystals of $[(\mathrm{PhCN_2S_2})_2\mathrm{AlCl_4}][\mathrm{S_3N_3}]$, $[\mathrm{S_5N_5}][\mathrm{AlCl_4}]$ was treated with $(\mathrm{PhCN_2S_2})_2$ in acetonitrile, using a typical crystal-growth procedure. After 1 week the products were isolated and identified by i.r. spectroscopy as $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$, and $[\mathrm{PhCN_2S_2}][\mathrm{AlCl_4}]$. as in equation (2). In contrast to the reaction with $[\mathrm{S_5N_5}]\mathrm{Cl}$, the $[\mathrm{AlCl_4}]^-$ anion appears to be too large and 'hard' to interact effectively with two $[\mathrm{PhCN_2S_2}]^+$ ions, thus avoiding precipitation of $[(\mathrm{PhCN_2S_2})_2\mathrm{AlCl_4}][\mathrm{S_3N_3}]$.

$$[\mathrm{S_5N_5}][\mathrm{AlCl_4}] \xrightarrow[-[\mathrm{PhCN_2S_2}][\mathrm{AlCl_4}]]{(\mathrm{PhCN_2S_2})_2} [\mathrm{PhCN_2S_2}^{\bullet} + \mathrm{S_5N_5}^{\bullet}] \longrightarrow [\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}] + \tfrac{1}{2}\mathrm{S_4N_4} \quad (2)$$

The $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$ crystals produced were large (up to 2 mm in length) and well formed. Although $[\mathrm{PhCN_2S_2}]^+$ and $[\mathrm{S_3N_3}]^-$ are electron-pair species (6 and 10π respectively), samples of $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$ showed a strong powder e.s.r. signal typical for that of $(\mathrm{PhCN_2S_2})_2$.[41] This does not appear to be due to contamination, as single-crystal measurements show the spectra to be strongly orientation dependent.[42] The presence of such a signal (corresponding to *ca.* 1% excess of $\mathrm{PhCN_2S_2}^{\bullet}$)[42] is likely to originate from crystal-lattice defects which could incorporate small amounts of monomeric $[\mathrm{PhCN_2S_2}]^{\bullet}$.

Mixing Vapours of $(\mathrm{SN})_x$ *and* $(\mathrm{Ph\overline{CNSSN}})_2$ *to produce* $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$ (3).—There has been much interest in the vapour species volatilised from $(\mathrm{SN})_x$, with earlier workers[43] suggesting linear $(\mathrm{SN})_4$ as the predominant species. Despite more recent studies, doubts still remain as to which vapour species hold the key role in the polymer formation. Besenyei *et al.*[44] suggested that $(\mathrm{SN})_2$ and $\mathrm{SN}^{\bullet}$ species were the main building blocks in $(\mathrm{SN})_x$ formation. On the other hand, Lau *et al.*[24] showed by He I photoelectron spectroscopy and *in situ* mass spectrometry that the vapour above $(\mathrm{SN})_x$ *in vacuo* at 130—150 °C is comprised mainly of $\mathrm{S_3N_3}^{\bullet}$ radicals. *Ab initio* calculations further showed that this $\mathrm{S_3N_3}^{\bullet}$ radical is most likely to be a planar ring. On this basis it was thought that $(\mathrm{SN})_x$ vapour might react with $(\mathrm{PhCN_2S_2})_2$ vapour producing $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$ as shown in equation (3).

$$\mathrm{S_3N_3}^{\bullet} + \tfrac{1}{2}(\mathrm{PhCN_2S_2})_2 \longrightarrow [\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}] \quad (3)$$

Indeed when the vapours of $(\mathrm{SN})_x$ (heated at 160 °C) and $(\mathrm{PhCN_2S_2})_2$ (heated at 50 °C) were mixed *in vacuo* (3×10^{-6} Torr), by passing through quartz wool at 160 °C, and products collected on a cold-finger at −196 °C, $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$ and $\mathrm{S_4N_4}$ [normally produced whenever $(\mathrm{SN})_x$ is vacuum sublimed] were produced, together with some unreacted $(\mathrm{PhCN_2S_2})_2$ and $(\mathrm{SN})_x$. The source temperatures for $(\mathrm{PhCN_2S_2})_2$ and $(\mathrm{SN})_x$ were chosen so as to obtain a favourable ratio of the mass flow of both components; the purpose of the quartz wool was to enhance mixing and the frequency of collisions. Only small amounts of $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_3}]$ were produced in the absence of quartz wool, the other materials on the cold-finger being starting materials.

We believe this result provides strong evidence that cyclic $\mathrm{S_3N_3}^{\bullet}$ is the main species in the vapour phase above $(\mathrm{SN})_x$; however, it is not entirely conclusive as SN monomer and $(\mathrm{SN})_2$ could be the initial vapour species which react 'in flight' to produce $\mathrm{S_3N_3}^{\bullet}$, hence the higher yield when the mean path length is increased by the incorporation of the quartz wool. It is less likely that linear $(\mathrm{SN})_4$ molecules are the initial vapour species.

Preparation of $[\mathrm{PhCN_2S_2}]_2\mathrm{Cl}$.—When $(\mathrm{PhCN_2S_2})_2$ and $[\mathrm{PhCN_2S_2}]\mathrm{Cl}$ (in a 1:2 molar ratio) were thoroughly ground together [equation (4)] and heated under a blanket of nitrogen, a brown solid was formed which was shown by elemental analysis, i.r. and mass spectroscopy to be $[\mathrm{PhCN_2S_2}]_2\mathrm{Cl}$.

$$(\mathrm{PhCN_2S_2})_2 + 2[\mathrm{PhCN_2S_2}]\mathrm{Cl} \longrightarrow 2[\mathrm{PhCN_2S_2}]_2\mathrm{Cl} \quad (4)$$

The solid e.s.r. spectrum (Figure 11) showed a single intense broad peak, which was not orientation dependent in a single crystal, indicating the presence of a relatively mobile radical. This new compound can be thought of as a mixture of $[\mathrm{PhCN_2S_2}]^+\mathrm{Cl}^-$ and $\mathrm{PhCN_2S_2}^{\bullet}$, the electron probably exchanging between CN_2S_2 rings in each molecule giving a resonance structure of $[PhCN_2S_2^{\frac{1}{2}+\frac{1}{2}\cdot}]_2Cl^-$. A similar compound, $(CF_3CN_2S_2)_3Cl$ (reported by Mews and co-workers[45]) consisting of a central Cl^- surrounded by three $CF_3CN_2S_2$ units, also gave an e.s.r. spectrum.

Extraction of $[PhCN_2S_2]_2Cl$ in acetonitrile produced a mixture of $(PhCN_2S_2)_2$ (soluble) and $[PhCN_2S_2]Cl$ (insoluble on the frit) suggesting that an equilibrium [equation (5)] between all three compounds exists; indeed, in the crystal-growth experiments carried out in acetonitrile, all three compounds were observed.

$$[PhCN_2S_2]Cl + \tfrac{1}{2}(PhCN_2S_2)_2 \rightleftharpoons [PhCN_2S_2]_2Cl \quad (5)$$

In this work we have shown (*i*) the value of $(PhCN_2S_2)_2$ for dehalogenation/ring contraction reactions of S/N/Cl compounds, (*ii*) the ease with which crystals of sparingly soluble compounds can be grown for *X*-ray analysis by slow diffusion methods in a simple apparatus, and (*iii*) how $(PhCN_2S_2)_2$ can be used to trap the $S_3N_3^{\cdot}$ radical from the vapour species generated above heated $(SN)_x$ *in vacuo*. The perturbations of bond distances in $PhCN_2S_2^+$ compounds due to interaction with donor anions have also been discussed.

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