

An Inorganic Heterocycle Containing an Exocyclic Sulphur–Iodine Bond: Synthesis and X-Ray Crystal Structure of $(\text{Ph}_2\text{PN})_2\text{NSI}$ and its Thermal Conversion into a Spirocyclic P_4SN_6 Ring

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The reaction of $(\text{Ph}_2\text{PN})_2\text{NSCl}$ with KI in acetonitrile produces $(\text{Ph}_2\text{PN})_2\text{NSI}$ which is shown by X-ray crystallography to contain a six-membered P_2SN_3 ring with an exocyclic S–I bond; the thermal decomposition of $(\text{Ph}_2\text{PN})_2\text{NSI}$ leads to $\text{Ph}_8\text{P}_4\text{SN}_6$, a spirocyclic compound in which two P_2SN_3 rings share a common sulphur atom.

The ionic compound $\text{S}_4\text{N}_3^+\text{I}^-$ is unstable above 0°C ,^{1,2} and this thermal instability has been used to advantage in the synthesis of S_4N_4 from thiazyl chlorides and sodium iodide.³ The existence of a covalent sulphur–iodine bond in thiazyl (S–N) compounds has not been unequivocally established.^{2,4,5} We report the preparation and X-ray crystal structure of $(\text{Ph}_2\text{PN})_2\text{NSI}$, (**1**), an inorganic heterocycle with an exocyclic sulphur–iodine bond which decomposes at *ca.* 150°C to give the spirocyclic compound, $\text{Ph}_8\text{P}_4\text{N}_6\text{S}$ (**2**).

The treatment of $(\text{Ph}_2\text{PN})_2\text{NSCl}$ ⁶ (2.1 mmol) with finely powdered potassium iodide (2.1 mmol) in dry acetonitrile (25 ml) at 23°C under nitrogen for 5 h produced (**1**) in *ca.* 85% yield. Potassium chloride (2.0 mmol) was separated by washing with methylene dichloride. The red crystals of (**1**) are

moisture-sensitive and give $[\text{H}_2\text{NPPPh}_2\text{NPPPh}_2\text{NH}_2]^+\text{I}^-$ on hydrolysis. The ^{31}P { ^1H } n.m.r. spectrum (in CDCl_3) shows a singlet at +9.9 p.p.m. (ref. external 85% H_3PO_4). Crystals of (**1**) suitable for an X-ray structural determination were obtained from methylene dichloride–acetonitrile (1:1).

Crystal data: $\text{C}_{24}\text{H}_{20}\text{IN}_3\text{P}_2\text{S}\cdot\text{CH}_3\text{CN}$ (**1**), $M = 612.4$, monoclinic, space group $P2_1$, $a = 11.451(2)$, $b = 7.710(1)$, $c = 15.335(3)$ Å, $\beta = 95.69(1)^\circ$, $U = 1347.2(4)$ Å³, $Z = 2$, $\mu(\text{Mo-K}_\alpha) = 14.19$ cm⁻¹, and $D_c = 1.51$ g cm⁻³. The intensity data were collected on a CAD4F diffractometer operating in the ω - 2θ mode and using Mo- K_α radiation ($\lambda = 0.7107$ Å, graphite monochromator). A total of 4178 unique reflections were measured at $23(3)^\circ\text{C}$, and 1792 of these had $I > 3\sigma(I)$. The structure was solved by direct methods (MULTAN 78)

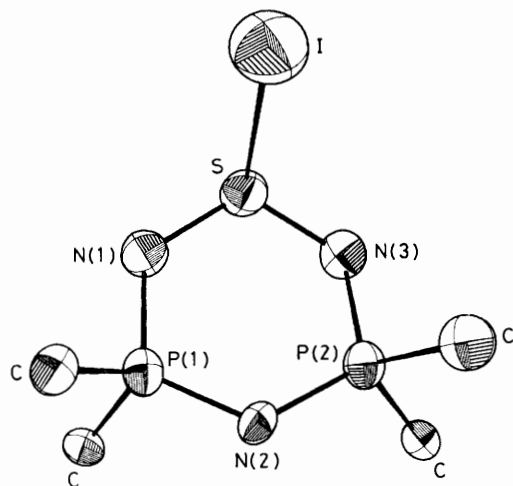


Figure 1. ORTEP plot (50% probability ellipsoids) for $(\text{Ph}_2\text{PN})_2\text{NSI}$, (1), showing the atomic numbering scheme. For clarity only the α -C atoms of the phenyl rings are shown. Principal bond distances (e.s.d.s in parentheses) are: S–N(1) 1.556(7); S–N(3) 1.544(7); N(1)–P(1) 1.667(9); N(3)–P(2) 1.656(9); N(2)–P(1) 1.590(7); N(2)–P(2) 1.582(7) Å. Principal bond angles are: N(1)–S–N(3) 116.8(4); S–N(1)–P(1) 121.5(5); S–N(3)–P(2) 122.5(5); N(1)–P(1)–N(2) 115.7(3); N(3)–P(2)–N(2) 114.3(3); P(1)–N(2)–P(2) 124.8(3)°.

and refined by full matrix least-squares techniques to give R 0.048 and R_w 0.040 for 2910 contributing reflections [reflections with $I < 3\sigma(I)$ were included in the refinement if $F_o > \sigma(F_o)$]. The weights were defined as $[\sigma(F_o)]^{-2}$.†

The structure of (1) is shown in Figure 1. The five atom NPNPN unit is planar to within 0.05 Å, while the sulphur atom lies *ca.* 0.29 Å out of this plane. The conformation and the endocyclic bond lengths and bond angles of the six-membered P_2SN_3 ring in (1) are similar to those found for the corresponding chloride, $(\text{Ph}_2\text{PN})_2\text{NSCl}$,⁶ and no further comment is warranted here. The most significant structural feature is the exocyclic sulphur–iodine bond [S–I 2.713(3) Å]. There are very few examples of structurally characterized compounds containing two-electron two-centre sulphur–iodine bonds with which to compare this value.⁷ However, the S–I distances in various salts of the S_7I^+ cation fall within the range 2.32–2.39 Å,⁸ which is close to the sum of the covalent radii for sulphur (1.04 Å) and iodine (1.33 Å).⁹ Thus it appears that there is a significant ionic contribution to the S–I bond in (1).

In view of the known tendency of iodide ion to reduce thiazyl chlorides,³ it is worth noting that the reaction of $(\text{Ph}_2\text{PN})_2\text{NSCl}$ with potassium iodide involves a simple substitution whereas reduction to a twelve-membered ring with a transannular S–S bond occurs with triphenylantimony.¹⁰ Compared to other thiazyl iodides,^{1–5} (1) has considerable thermal stability. However, it does decompose at *ca.* 150 °C to give a colourless, crystalline solid (2), m.p. 231 °C, as the major product. The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum of (2) (in CDCl_3) shows a sharp singlet at +17.9 p.p.m. The dominant feature in the mass spectrum of (2) is the molecular ion (m/z 856). Crystals suitable for an X-ray structural determination were obtained from acetonitrile.

Crystal data: $\text{C}_{48}\text{H}_{40}\text{N}_6\text{P}_4\text{S} \cdot 1/2\text{CH}_3\text{CN}$, $M = 877.4$, triclinic, space group $\bar{P}1$, $a = 13.691(1)$, $b = 18.168(2)$, $c =$

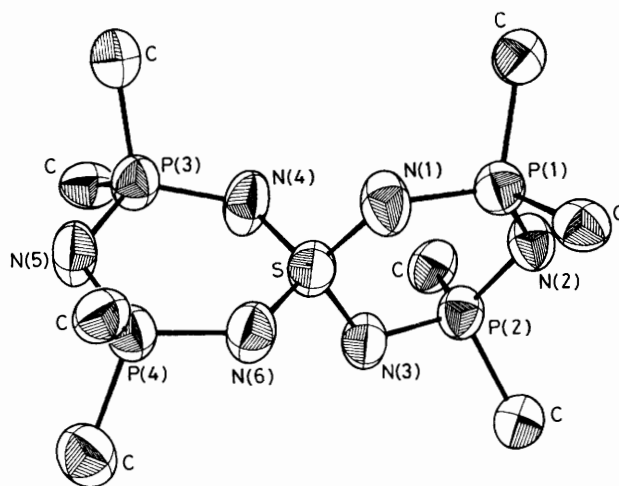


Figure 2. ORTEP plot (50% probability ellipsoids) for $(\text{Ph}_2\text{PN})_2\text{N}_2\text{S}$, (2), showing the atomic numbering scheme. For clarity only the α -C atoms of the phenyl rings are shown. Principal bond distances are: S–N(1) 1.556(4); S–N(3) 1.560(3); S–N(4) 1.565(3); S–N(6) 1.553(4); N(1)–P(1) 1.604(4); P(1)–N(2) 1.587(3); N(2)–P(2) 1.584(4); P(2)–N(3) 1.609(4); N(4)–P(3) 1.592(4); P(3)–N(5) 1.593(4); N(5)–P(4) 1.589(3); P(4)–N(6) 1.594(4) Å. Principal bond angles are: N(1)–S(1)–N(6) 107.0(2); N(1)–S(1)–N(3) 111.9(2); N(3)–S(1)–N(4) 108.7(2); N(4)–S(1)–N(6) 112.5(2); S(1)–N(1)–P(1) 125.3(2); N(1)–P(1)–N(2) 116.3(2); P(1)–N(2)–P(2) 120.1(2); N(2)–P(2)–N(3) 116.3(2); P(2)–N(3)–S(1) 121.4(2); S(1)–N(4)–P(3) 125.5(3); N(4)–P(3)–N(5) 117.0(2); P(3)–N(5)–P(4) 119.6; N(5)–P(4)–N(6) 117.0(2); P(4)–N(6)–S(1) 126.8(2)°. These parameters are for one of the molecules in the asymmetric unit. The bond lengths and bond angles for the second molecule do not differ significantly.

19.032(2) Å, $\alpha = 104.572(8)$, $\beta = 92.867(7)$, $\gamma = 97.613(8)$ °, $U = 4525(1)$ Å³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 2.57$ cm⁻¹, $D_c = 1.29$ g cm⁻³, and $D_m = 1.30$ g cm⁻³ (floatation in CCl_4 –hexane). A total of 8420 unique reflections, of which 5627 had $I > 3\sigma(I)$, were measured at 23(3) °C using Mo–K α radiation. With $Z = 4$, the asymmetric unit consists of two independent molecules of (2) and one molecule of MeCN solvate. The structure was solved by direct methods and has been refined to R 0.038 and R_w 0.051 for 7290 contributing reflections. The weights were defined as $[\sigma(F_o)]^2 + 0.001F_o^3$.†

The structure of one molecule of (2) is illustrated in Figure 2. It consists of two almost planar six-membered P_2SN_3 rings fused at a common (spirocyclic) sulphur atom.‡ The geometry at this sulphur atom is approximately tetrahedral with bond angles in the range 105–113° and the four S–N bond lengths are equal (mean value 1.56 Å). Thus (2) differs from the related spirocycle with eight-membered $\text{P}_2\text{S}_2\text{N}_4$ rings which has two pairs of S–N bond lengths (at the spirocyclic sulphur atom) of *ca.* 1.61 and *ca.* 1.56 Å.⁶ In the latter compound the two eight-membered rings are linked by an S–S bond, probably because the individual $\text{P}_2\text{S}_2\text{N}_4$ rings are π -electron rich [cf. 1,5- $\text{R}_2\text{P}(\text{NSN})_2\text{PR}_2$; R = Me,¹¹ Ph¹²]. In (2), however, each six-membered P_2SN_3 ring would be formally associated with six π -electrons (assuming sulphur contributes one π -electron to each ring). Thus the P_2SN_3 rings are π -electron precise¹⁰ [cf. cyclotriphosphazenes (P_3N_3)]. This may account for the high thermal stability of (2), which is the final product of many thermal transformations involving PNS heterocycles.¹³ It is interesting to note that an anionic spirocyclic phosphazene, $\text{R}_8\text{P}_5\text{N}_6^-$, formally isoelectronic with (2), has

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ The deviations from the best plane through all atoms of each six-membered ring are 0.048 and 0.103 Å for molecule A and 0.088 and 0.099 Å for molecule B.

been reported but the X-ray crystal structure was not determined.^{14,15} The P-N bond lengths of 1.59–1.61 Å in (2) are typical for cyclophosphazenes.¹⁶

The mechanism of the transformation of six-membered P₂SN₃ rings to the spirocyclic compound, (2), which involves the intermediate formation of a twelve-membered ring, is described in the following communication.¹³

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