

## Formation and X-Ray Structural Characterization of a Twelve-membered $P_4S_2N_6$ Ring in the Thermal Conversion of a $P_2SN_3$ Ring into the $P_4SN_6$ Spirocycle

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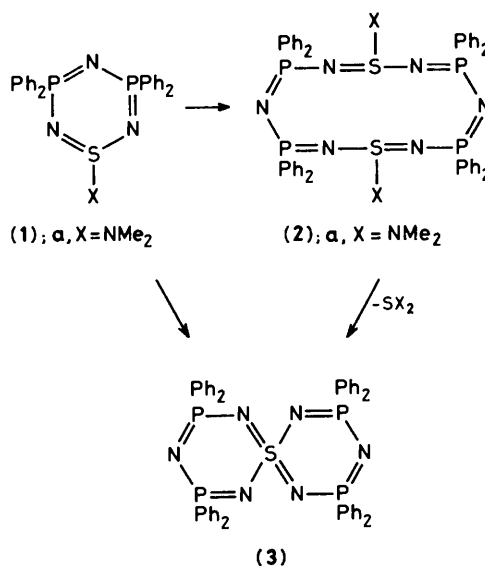
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The thermal conversion of  $(Ph_2PN)_2NSNMe_2$  at 150–185 °C into the spirocyclic compound  $Ph_8P_4N_6S$  occurs via a twelve-membered ring whose structure has been determined by X-ray crystallography.

We have recently reported that six-membered rings of the type  $(Ph_2PN)_2NSX$  (**1**,  $X = Cl, I$ ) undergo thermal decomposition at 150–200 °C to give the spirocyclic compound (**3**).<sup>1</sup> We now describe the formation and X-ray structural determination of a twelve-membered ring (**2a**), ( $X = NMe_2$ ) formed as an intermediate in the thermal transformation of (**1a**) ( $X = NMe_2$ ) to (**3**).

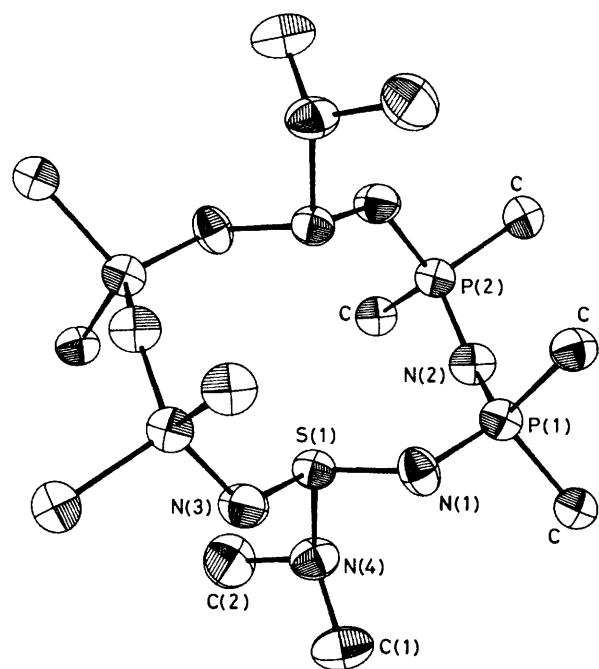
The reaction of  $(Ph_2PN)_2NSCl^2$  (2.1 mmol) with  $Me_3SiNMe_2$  (3.0 mmol) in dry methylene dichloride (25 ml) at 23 °C for 2 h gave pale yellow crystals of  $(Ph_2PN)_2NSNMe_2$  (1.8 mmol), m.p. 135 °C decomp. The  $^{31}P\{^1H\}$  n.m.r. spectrum of (**1a**) (in  $CDCl_3$ ) shows a singlet at +7.8 p.p.m. (ref. external 85%  $H_3PO_4$ ). After several days at 23 °C a solution of (**1a**) in acetonitrile produces colourless crystals of (**2a**) which were used in an X-ray structure determination. Compound (**2**) has m.p. 175 °C decomp. and the  $^{31}P\{^1H\}$  n.m.r. spectrum exhibits a singlet at +5.0 p.p.m.

*Crystal data:*  $C_{52}H_{52}N_8P_4S_2$  (**2**),  $M = 977.1$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.8143(9)$ ,  $b = 10.8406(9)$ ,  $c = 12.5523(4)$  Å,  $\alpha = 79.082(5)$ ,  $\beta = 67.657(5)$ ,  $\gamma = 65.821(7)^\circ$ ,  $U = 1240.7(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $\mu(Cu-K\alpha) = 24.93$  cm<sup>-1</sup>, and  $D_c = 1.31$  g cm<sup>-3</sup>. With  $Z = 1$  a crystallographic centre of symmetry is imposed on the molecule. The intensity data were collected on a CAD4F diffractometer operating in the  $\omega-2\theta$  mode and using  $Cu-K\alpha$  radiation ( $\lambda = 1.5418$  Å, Ni prefilter). A total of 5108 unique reflections were measured at 23(3) °C of which 3276 had  $I > 3\sigma(I)$ . The structure was solved by direct methods (MULTAN 78) and refined by full matrix least-squares techniques on  $F$  to



give  $R$  0.047 and  $R_w$  0.051 (298 variables and 3276 observations). Unit weights were used to calculate  $R_w$ .†

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



**Figure 1.** ORTEP plot (50% probability ellipsoids) for  $(\text{Ph}_2\text{PN})_4(\text{NSNMe}_2)_2$  (**2a**), showing the atomic numbering scheme. For clarity only the  $\alpha$ -C atoms of the phenyl rings are shown. Principal bond distances (e.s.d.s in parentheses) are S(1)–N(1) 1.585(5); S(1)–N(3) 1.596(3); S(1)–N(4) 1.703(3); N(1)–P(1) 1.610(3); P(1)–N(2) 1.570(4); N(2)–P(2) 1.578(3); P(2)–N(3) 1.601(3); N(4)–C(1) 1.465(6); N(4)–C(2) 1.458(9) Å. Principal bond angles are: P(2)–N(2)–P(1) 148.3(2); N(2)–P(1)–N(1) 119.5(2); P(1)–N(1)–S(1) 120.6(2); S(1)–N(3)–P(2) 122.0(2); N(3)–P(2)–N(2) 122.3(2); N(1)–S(1)–N(3) 105.0(2); N(1)–S(1)–N(4) 103.4(2); N(4)–S(1)–N(3) 102.6(2); C(1)–N(4)–S(1) 114.4(4); C(1)–N(4)–C(2) 113.1(4); C(2)–N(4)–S(1) 109.1(3)°.

The structure of (**2a**) is shown in Figure 1. It consists of a twelve-membered  $\text{P}_4\text{S}_2\text{N}_6$  ring with a *trans* dimethylamino substituent on each of the two sulphur atoms. The endocyclic S–N bond lengths [mean value 1.590(5) Å] are considerably shorter than the exocyclic bond length of 1.703(3) Å which is close to the value expected for an  $\text{S}^{\text{IV}}$ –N single bond. In contrast, the exocyclic S–N bond [1.590(4) Å] in the related dialkylamino-substituted thiaziazines is significantly shorter than the endocyclic S–N bonds [1.655(3) Å].<sup>3</sup> The S–N bond lengths and the pyramidal geometry at N(4) [mean bond angle 112.2(4)°] suggest that there is very little  $\pi$ -bonding between the exocyclic nitrogen atom and S(1) in (**2a**). In the related molecule 1,5-( $\text{Me}_2\text{N}$ )<sub>2</sub> $\text{S}_4\text{N}_4$  a significant transannular interaction between the dimethylamino nitrogens and opposite sul-

**Table 1.** Distribution of products in the thermolysis of  $(\text{Ph}_2\text{PN})_2\text{-NSNMe}_2$ .<sup>a</sup>

Temp./°C	t/h	Weight of products/mg <sup>b</sup>	
		( <b>2a</b> )	( <b>3</b> )
100	1.5	— <sup>c</sup>	— <sup>c</sup>
125	1.5	12	trace
150	0.5	25	10
185	0.5	— <sup>c</sup>	59

<sup>a</sup> Carried out under a dynamic vacuum (*ca.*  $10^{-2}$  Torr) using 70 mg of (**1a**). <sup>b</sup> The products were separated by treatment with acetonitrile in which (**2a**) is insoluble. <sup>c</sup> Not detected.

phur atoms (S–N 2.760 Å) was observed in the solid state structure.<sup>4,5</sup> In (**2a**), however, the *trans* orientation of the dimethylamino substituents precludes any such interaction.

We have reported previously that ring opening reactions occur readily for  $\text{P}_2\text{SN}_3$  heterocycles containing three coordinate sulphur.<sup>2,6</sup> In the present example, the conversion of (**1a**) into (**2a**) can be accelerated by controlled heating of a pure sample of (**1a**) (see Table 1). The final product of this thermolysis is the spirocyclic compound (**3**), which is formed almost quantitatively when (**2a**) is heated at 180 °C for 2 h. Presumably, the flexibility of the twelve-membered ring allows the formation of a transition state from which  $(\text{R}_2\text{N})_2\text{S}$ , an identified by-product of this thermolysis, can be readily eliminated.

Compound (**2a**) is the first example of a ring system with more than eight atoms<sup>7</sup> in the mixed phosphazene–thiazyl series  $(\text{R}_2\text{PN})_x(\text{NSR}')_y$ . As such it provides evidence to support the contention that this class of inorganic heterocycles is potentially extensive.<sup>2</sup>

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