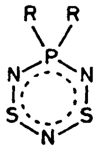
Preparation and *X*-Ray Crystal Structure of 3,3,5,5,9,9,11,11-Octaphenyl-1,7-di-λ^4-thia-2,4,6,8,10,12-hexa-aza-3,5,9,11-tetra-λ^5-phosphabicyclo[5.5.0]dodecahexaene: a Twelve-membered Inorganic Heterocycle with a Transannular Sulphur–Sulphur Bond

Tristram Chivers,* M. N. Sudheendra Rao, and John F. Richardson

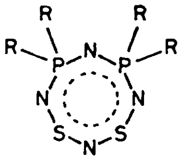
Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

The reaction of the six-membered ring compound $(Ph_2PN)_2NSCl$ with triphenylantimony in acetonitrile produces $(Ph_2PN)_4(SN)_2$ shown by *X*-ray crystallography to consist of a twelve-membered ring with a transannular sulphur–sulphur bond.

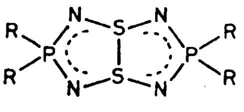
A variety of ring sizes is known for π-electron rich, binary sulphur–nitrogen species containing two-co-ordinate sulphur *e.g.* S_2N_2, $S_3N_3^-$, $S_4N_4^{2+}$, and $S_5N_5^+$.[1] An even broader range of ring sizes is found for the π-electron-precise† inorganic heterocycles known as cyclophosphazenes, $(R_2PN)_x$ (x = 3—17).[2] We have recently prepared and structurally characterized cyclophosphathiazenes of the type $(R_2PN)_n(SN)_2$:[3—5] (**1**, n = 1) an eight π-electron system,[3] (**2**, n = 2) a ten π-electron system,[5] and (**3**, n = 2) a bicyclic compound with a transannular sulphur–sulphur bond.[4,5] The existence of higher members of this homologous series was suggested[5] and we now report the preparation and *X*-ray crystal structure of a twelve-membered ring (n = 4).



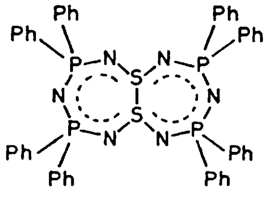
(**1**)



(**2**)



(**3**)



(**4**)

The treatment of $(Ph_2PN)_2NSCl$[6] (2.71 mmol) with triphenylantimony (1.36 mmol) in acetonitrile (25 ml) at 23 °C under nitrogen for 24 h produced $(Ph_2PN)_4(SN)_2$ (**4**) in *ca.* 40% yield as a bright yellow precipitate which was recrystallized from methylene dichloride–acetonitrile (1 : 1), m.p. 182—184 °C.‡ Triphenylantimony dichloride and small amounts of (**2**) and (**3**) were isolated from the filtrate.

The $\{^1H\}^{31}P$ n.m.r. spectrum of (**4**) in $CDCl_3$ shows a sharp singlet at +15.3 p.p.m. (ref. external 85% H_3PO_4). The Raman spectrum exhibits three strong bands at 370, 308, and 245 cm^{-1} in the region expected for weak cross-ring sulphur–sulphur bonds in sulphur–nitrogen cages or bicyclic molecules.[4]

---

† This term implies that π-bonding levels are fully occupied and π^*-levels are unoccupied, in contrast to the cyclic S–N compounds in which π^*-levels are partially occupied (π-electron rich).

‡ Elemental analyses for C, H, N, S, and P (by difference) were in excellent agreement with the empirical formula $(Ph_2PN)_2NS$ and the base peak in the mass spectrum had m/z 444 corresponding to the positive ion of this monomer unit. However, peaks were also observed at m/z 888 (<1%) and 856 (8%) corresponding to the dimer and loss of one sulphur from the dimer, respectively.

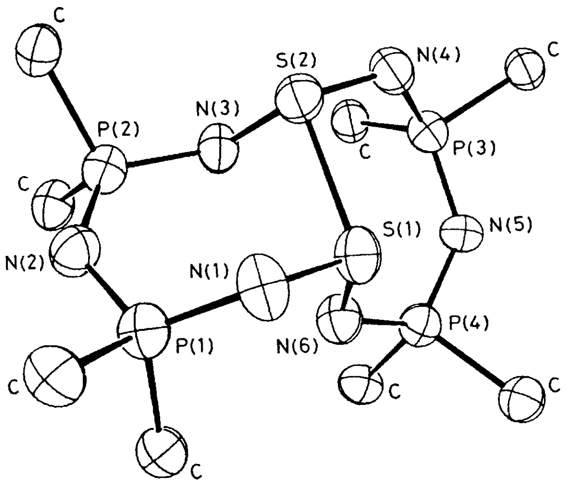


Figure 1. A perspective drawing (50% probability ellipsoids) for $(Ph_2PN)_4(SN)_2$, (**4**), showing the atomic numbering scheme. For clarity only the α-C atoms of the phenyl rings are shown. Principal bond distances (e.s.d.s. in parentheses) are: S(1)–S(2), 2.385(1); S(1)–N(1), 1.596(2); N(1)–P(1), 1.624(2); P(1)–N(2), 1.580(3); N(2)–P(2), 1.582(3); P(2)–N(3), 1.614(2); N(3)–S(2), 1.603(2); S(2)–N(4), 1.594(2); N(4)–P(3), 1.626(3); P(3)–N(5), 1.584(3); N(5)–P(4), 1.583(2); P(4)–N(6), 1.613(2); N(6)–S(1), 1.599(3) Å. Principal bond angles are: S(2)–S(1)–N(1), 102.7(1); S(2)–S(1)–N(6), 97.3(1); N(6)–S(1)–N(1), 107.8(1); S(1)–N(1)–P(1), 123.4(2); N(1)–P(1)–N(2), 118.7(1); P(1)–N(2)–P(2), 134.0(1); N(2)–P(2)–N(3), 120.5(1); P(2)–N(3)–S(2), 120.8(2); N(3)–S(2)–S(1), 97.1(1); N(3)–S(2)–N(4), 109.5(1); S(1)–S(2)–N(4), 101.8(1); S(2)–N(4)–P(3), 126.5(1); N(4)–P(3)–N(5), 120.7(1); P(3)–N(5)–P(4), 132.9(1); N(5)–P(4)–N(6), 118.4(1); P(4)–N(6)–S(1), 121.5(1)°.

Yellow platelets of (**4**) suitable for an *X*-ray structural determination were obtained from methylene dichloride–diethyl ether.

Crystal data: (**4**), $C_{48}H_{40}N_6P_4S_2$, $M = 888.9$, triclinic, space group $P\bar{1}$, $a = 9.191(1)$, $b = 11.724(1)$, $c = 21.409(2)$ Å, $\alpha = 79.294(8)$, $\beta = 89.015(9)$, $\gamma = 75.299(10)^\circ$, $U = 2191.5(6)$ Å^3, $Z = 2$, $D_c = 1.347$ g cm^{-3}. A total of 7676 unique reflections were measured at 23 °C of which 4559 had $I \geqslant 3\sigma(I)$. The data were collected on a CAD4F diffractometer operating in the ω—2θ mode and using Mo-K_α radiation ($\lambda = 0.71069$ Å; graphite monochromator). The structure was solved by direct methods (MULTAN 78) and refined by full-matrix least-squares techniques on F to give a final R-value of 0.046 ($R_w = 0.024$) for 6216 contributing reflections [reflections with $I < 3\sigma(I)$ were included in the refinement if $F_c >$ threshold].§ The weighting scheme used was $w = [\sigma^2(F_o)]^{-1}$.

As indicated in Figure 1, the structure of (**4**) consists of a twelve-membered ring with a transannular S–S interaction. Alternatively it may be regarded as a bicyclic molecule in which two 7-membered rings share a common S–S bond [*d*(S–S) = 2.385(1), *cf.* 2.528(1) Å in (**3**; R = Ph)].[5] The mean S–N bond length in (**4**) of 1.598(2) Å is similar to that found for (**3**) [1.590(3) Å] and the mean P–N bond lengths of the NPNPN unit [1.582(3) (internal) and 1.619(3) Å (terminal)] are indistinguishable from those found for the 1,3-isomer (**2**) [1.587(3) and 1.613(3), respectively].[5] The two rings in (**4**) adopt a *cis*-configuration about the S–S bond. However, in contrast to the structure of (**3**),[4,5] the geometry about the S–S bond is considerably twisted as a result of the introduction of an additional Ph_2PN unit into each half of the bicyclic ring.

A planar monocyclic $P_4S_2N_6$ ring would have fourteen π-electrons, *cf.* $S_5N_5^+$.[7] Although it is tempting to suggest that the formation of a transannular S–S σ-bond in (**4**) is sufficient to outweigh the greater π-delocalisation energy of the planar ring [*cf.* 1,5-$R_2P(NSN)_2PR_2$],[4,5] it seems likely that other factors also contribute to the observed geometry.

The structural characterization of (**4**) confirms the suggestion that rings containing more than eight atoms are possible for cyclophosphathiazenes containing two-co-ordinate sulphur and serves to emphasize that ring-opening reactions are an important feature of the chemistry of the P_2SN_3 ring.[6]

We thank the Natural Sciences and Engineering Research Council (Canada) for financial support.

Received, 22nd November 1982; Com. 1332

References

1 H. W. Roesky, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 239; R. Gleiter, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 444; T. Chivers and R. T. Oakley, *Top. Curr. Chem.*, 1982, **102**, 117.

2 S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 41.

3 N. Burford, T. Chivers, R. T. Oakley, A. W. Cordes, and P. N. Swepston, *J. Chem. Soc., Chem. Commun.*, 1980, 1204; N. Burford, T. Chivers, A. W. Cordes, W. G. Laidlaw, M. Noble, R. T. Oakley, and P. N. Swepston, *J. Am. Chem. Soc.*, 1982, **104**, 2182.

4 N. Burford, T. Chivers, P. W. Codding, and R. T. Oakley, *Inorg. Chem.*, 1982, **21**, 982.

5 N. Burford, T. Chivers, and J. F. Richardson, *Inorg. Chem.*, in the press.

6 T. Chivers, M. N. S. Rao, and J. F. Richardson, *J. Chem. Soc., Chem. Commun.*, 1982, 982.

7 R. Bartetzko and R. Gleiter, *Inorg. Chem.*, 1978, **17**, 995; R. Gleiter and R. Bartetzko, *Z. Naturforsch., Teil B*, 1981, **36**, 956.

---

§ 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.