Preparation and Crystal Structure of 1,1-Diphenyl-1-phospha-3,5-dithia-2,4,6-triazene, $Ph_2PS_2N_3$; an Eight π-electron Inorganic Heterocycle

By NEIL BURFORD, TRISTRAM CHIVERS,* and RICHARD T. OAKLEY
(*Department of Chemistry, The University of Calgary, Calgary T2N 1N4, Alberta, Canada*)
and A. WALLACE CORDES and PAUL N. SWEPSTON
(*Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701*)

Summary. The reaction of tetraphenyldiphosphine with S_4N_4 in toluene produces the six-membered heterocycle $Ph_2PS_2N_3$, the structure of which has been determined by X-ray crystallography; the structural parameters and electronic spectrum of the PS_2N_3 ring are consistent with an 8-electron π-system.

ALTHOUGH a number of planar S–N rings, *e.g.* S_2N_2 (6π),[1] $S_3N_3^-$ (10π),[2] $S_4N_4^{2+}$ (10π),[3] and $S_5N_5^+$ (14π)[4] follow the Hückel rule (for aromaticity), there are exceptions, *e.g.* $S_3N_2^+$ (7π),[5] and Banister has recently suggested that lack of strain may be more important than '$4n + 2$ stabilization' in promoting ring stability.[6] In a continuation of our studies of reactions of phosphines with S_4N_4,[7] we have found that tetraphenyldiphosphine reacts with S_4N_4 to produce $Ph_2PS_2N_3$ (**1**) shown by X-ray crystallography to contain a six-membered ring comprising one P, two S, and three N atoms. This heterocycle is a rare inorganic example of a 6-atom eight π-electron ring system.

Compound (**1**) was prepared by adding tetrasulphur tetranitride (6·68 mmol) to a solution of tetraphenyldiphosphine (6·70 mmol) in toluene (40 ml) under nitrogen. After 15 min at reflux the yellow solution had become intense red–purple. After 14 h the volume of solvent was reduced to 10 ml *in vacuo*, and chromatography of this solution on a Bio-Beads S-X8 column (30 × 500 mm) gave (**1**) (1·65 mmol) as lustrous, deep purple plates (m.p. 93—94 °C) after recrystallization from acetonitrile. The u.v.-visible spectrum of (**1**) shows bands at 550 (ϵ *ca.* 5×10^3 l mol^{-1} cm^{-1}), 301 (3×10^3), and 252 nm (6×10^3). The ^{31}P n.m.r. spectrum ($CDCl_3$) shows a singlet at δ —21·2 p.p.m. (*vs.* external H_3PO_4).

Crystals suitable for an X-ray structural determination were obtained from acetonitrile. *Crystal data*: $C_{12}H_{10}N_3PS_2$, $M = 291·3$, monoclinic, space group $P2_1/c$, $a = 8.305(1)$, $b = 13.183(2)$, $c = 12.487(1)$ Å, $\beta = 105.53(1)°$, $U = 1317.3$ Å^3, $Z = 4$, and $D_c = 1.47$ g cm^{-3}. A total of 1611 reflections [$I \geqslant 3\sigma(I)$] were collected with a manual GE XRD-5 diffractometer employing the θ–2θ technique with Ni-filtered Cu-K_α radiation. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares techniques and all non-hydrogen atoms were refined anisotropically to give a final unweighted R-factor of 0·047.†

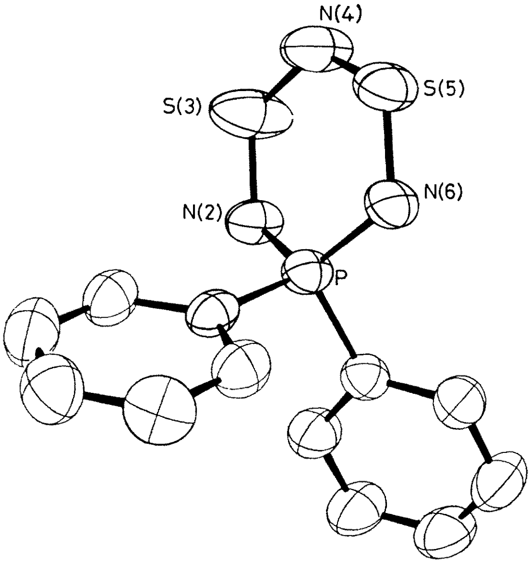

FIGURE 1. ORTEP drawing of $Ph_2PS_2N_3$ (**1**) showing the atomic numbering scheme. The atoms are represented by their thermal ellipsoids drawn to enclose 50% of their electron density. Hydrogen atoms are omitted for clarity. Principal bond distances (e.s.d.s in parentheses) are P(1)–N(2), 1·621(4), P(1)–N(6), 1·625(3), N(2)–S(3), 1·560(3), N(6)–S(5), 1·575(3), S(3)–N(4), 1·580(4), S(5)–N(4), 1·583(5) Å. Principal bond angles are N(6)–P(1)–N(2), 115·8(2), P(1)–N(2)–S(3), 121·3(2), P(1)–N(6)–S(5), 120·3(2), N(2)–S(3)–N(4), 116·9(2), N(4)–S(5)–N(6), 116·3(2), S(3)–N(4)–S(5), 124·6(3)°.

---

† 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.

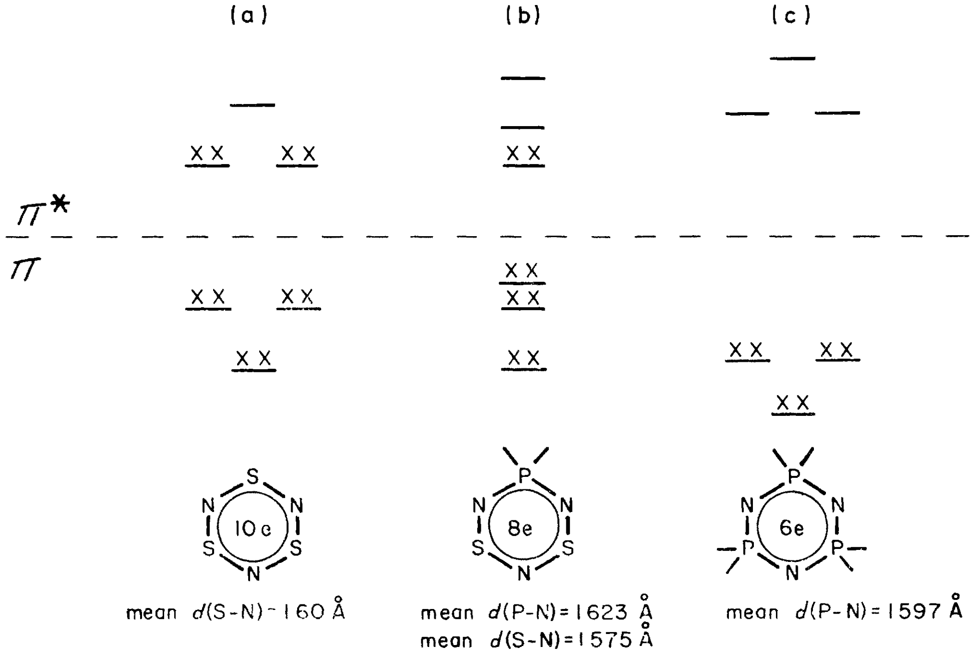

FIGURE 2 π-Energy level diagram (not to scale) for (a) $S_3N_3^-$, (b) $Ph_2PS_2N_3$ and (c) $(Ph_2PN)_3$ (assuming homomorphic interactions $\alpha_N = \alpha_S + 2\beta = \alpha_P + 3\beta$, all βs equal) The dashed line separates bonding and antibonding orbitals

The structure of (**1**) is shown in Figure 1 The five atoms N(2)–S(3)–N(4)–S(5)–N(6) are coplanar to within 0 05 Å, but the phosphorus atom is 0 28 Å out of this plane Thus the nearly planar conformation is in marked contrast to the structure of $(Me_3SiNH)_2PS_2N_3$, in which the six-membered ring is distinctly puckered and significant bond length variations are observed [8,9] The endocyclic bond lengths of the PS_2N_3 ring (an 8e π-system) in (**1**) provide an interesting comparison with those of the related $S_3N_3^-$ (a 10e π-system)[2] and $(Ph_2PN)_3$ (a 6e π-system)[10,11] structures The HMO π-energy levels for all three rings are illustrated in Figure 2 Thus the relatively long P–N and short S–N bonds in (**1**) reflect the mean P–N and S–N π-bond orders expected for a homomorphic π-system whose π* levels are occupied to an extent intermediate between those of $S_3N_3^-$ and $(Ph_2PN)_3$ The origin of the low-energy electronic excitation in (**1**) is also readily seen from Figure 2 The degenerate LUMO of $S_3N_3^-$ (for which the π → π* transition is at 360 nm)[2] is split in (**1**), giving rise to a small HOMO–LUMO gap Consistent with the large HOMO–LUMO gap in $(Ph_2PN)_3$, this latter molecule shows no absorption band above 200 nm

In summary, (**1**) is another example of a non-Huckel ring, which provides support for the conclusion that a $4n + 2$ complement of π-electrons is not associated with any special stabilization energy in electron-rich systems [6a,12,13] The important factor is the ability of the system to accommodate non-bonding and/or antibonding π-electrons in a relatively strain-free ring, *e g* $S_3N_3^-$,[2] $S_5N_5^+$,[14] by formation of a cage, *e g* S_4N_4,[12] or by dimerization, *e g* $S_6N_4^{2+}$ [15]

We thank the Natural Sciences and Engineering Research Council of Canada, the University of Calgary, and the University of Arkansas Research Committee for financial support

(*Received*, 16*th September* 1980, *Com* 1012)

[1] C M Mikulski, P J Russo, M S Saran, A G MacDiarmid, A F Garito, and A J Heeger, *J Am Chem Soc* , 1975, **97**, 6358

[2] J Bojes T Chivers, W G Laidlaw and M Trsic, *J Am Chem Soc* 1979, **101** 4517

[3] R J Gillespie D R Slim and J D Tyrer *J Chem Soc Chem Commun* , 1977 253

[4] H W Roesky, W Grosse-Bowing I Rayment and H M M Shearer, *J Chem Soc Chem Commun* , 1975 735, A J Banister, J A Durrant, I Rayment, and H M M Shearer *J Chem Soc Dalton Trans* , 1976, 928

[5] R J Gillespie P R Ireland and J E Vekris *Can J Chem* , 1975, **53** 3147, H W Roesky and A Hamza, *Angew Chem* , *Int Ed Engl* , 1976, **15**, 226

[6] (a) A J Banister and J A Durrant, *J Chem Research*, 1978, (*S*), 152, (*M*), 1931 (b) A J Banister, *Phosphorus and Sulfur*, 1979, **6**, 421

[7] J Bojes, T Chivers, G MacLean, R T Oakley, and A W Cordes, *Can J Chem* , 1979, **57**, 3171, J Bojes, T Chivers, A W Cordes, R T Oakley, and G MacLean, *Inorg Chem* , in the press

[8] R Appel and M Halstenberg, *Angew Chem* , *Int Ed Engl* , 1976, **15**, 696

[9] J Weiss, *Acta Crystallogr* , *Sect B*, 1977, **33**, 2272

[10] F R Ahmed, P Singh, and W H Barnes, *Acta Crystallogr* , *Sect B*, 1969, **25**, 316

[11] D P Craig and N L Paddock, *Nonbenzenoid Aromatics*, 1971, **2**, 273

[12] R Gleiter, *J Chem Soc* (*A*), 1970, 3174, R Bartetzko and R Gleiter, *Chem Ber* , 1980, **113**, 1138

[13] B M Gimarc and N Trinajstic, *Pure Appl Chem* , 1980, **52**, 1143

[14] R Bartetzko and R Gleiter, *Inorg Chem* , 1978, **17**, 995

[15] R Gleiter, B Bartetzko, and P Hofmann, *Z Naturforsch* , *Teil B*, 1980, **35**, 1166