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Structure of Tris(phenylthio)phosphine

By Neil Burford* and Bruce W. Royan

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

and Peter S. White*

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

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Abstract. $C_{18}H_{15}PS_3$, $M_r = 358{\cdot}47$, trigonal, $R\bar{3}$, $a = 12{\cdot}6760\ (12)$, $c = 18{\cdot}8921\ (20)$ Å, $V = 2628{\cdot}9\ (4)$ Å^3, $Z = 6$, $D_x = 1{\cdot}359$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}26$ mm^{-1}, $F(000) = 1116$, $T = 293$ K, $R = 0{\cdot}031$ for 899 significant reflections. The structure consists of discrete molecular units. The phosphine centre has pyramidal geometry and C_3 symmetry. The compound contains a rare example of a genuine P^{III}—S single bond with a bond length of 2·122 (1) Å. The C—S bond length is 1·785 (2) Å.

Introduction. Structural studies of the phosphorus(III)—sulfur single bond are rare and pertain almost exclusively to cyclic compounds (Tuzova, Naumov, Galiakberov, Ofitserov & Pudovik, 1981). Accurate determination of representative P—S bond lengths and geometry provides an important base comparison for the development of new bonding arrangements for phosphorus and sulfur (Burford, Royan, Linden & Cameron, 1988, 1989; Burford & Royan, 1989). Here we report the crystal structure of the title compound, a simple phosphine containing an example of a genuine strain-free P^{III}—S single σ bond.

Experimental. The title compound was prepared from thiophenol and $PhSPCl_2$ in ether (Moedritzer, Maier & Groenweghe, 1962). White, air-sensitive crystals were grown by slow evaporation of a CCl_4 solution. Crystal 0·60 × 0·60 × 0·35 mm (Pyrex capillary); Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice constants were obtained from 30 well centred reflections in the range $30 < 2\theta < 33°$. Intensities were measured using an $\omega/2\theta$ scan mode to $2\theta_{\max}$ of 50°, $h_{\max}$ 13, $k_{\max}$ 14, $l_{\max}$ 22. Three standard reflections monitored every hour showed no significant deviations in intensity. Intensities of 6127 reflections were measured and averaged to yield 1036 unique reflections ($R_{\text{int}} = 0{\cdot}018$) of which 899 were considered observed [$I > 2{\cdot}5\sigma(I)$]. Absorption corrections were made. The maximum and minimum transmission factors are 0·9073 and 0·9068. The structure was solved by direct methods and refined by full-matrix least squares minimizing $\sum w(\Delta F)^2$, where $w = 1/[\sigma(F)^2 + 0{\cdot}00005F^2]$ and σ was obtained from counting statistics. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and corrected for anomalous dispersion. All non-H atoms were refined anisotropically, the H atoms were located in a difference Fourier synthesis and refined isotropically with the temperature factor of the atom to which they are bound. The final cycles of refinement of 87 parameters gave $R = 0{\cdot}031$, $wR = 0{\cdot}045$ and a goodness of fit of 1·635. The largest Δ/σ was 0·118. A final difference synthesis showed no significant features and had a maximum of 0·20 e Å^{-3} and a minimum of −0·14 e Å^{-3}. All computations were performed using the PC version of *NRCVAX* (Gabe, Lee & Le Page, 1985). Table 1 lists refined fractional coordinates and Table 2 provides selected bond lengths and angles.† An *ORTEP* (Johnson, 1976) view of the molecular unit and a *PLUTO* (Motherwell & Clegg, 1978) stereoview of the unit-cell contents are displayed in Figs. 1 and 2, respectively.

Discussion. The structure consists of discrete molecular units, the phosphorus centres of which reside on a crystallographic threefold axis. The PS_3 unit adopts the standard pyramidal geometry, and the phenyl groups assume a *cis* orientation with respect to the lone pair on phosphorus (*exo* configuration). The compound is isostructural with the arsenic analogue $(PhS)_3As$ (Pappalardo, Chakravorty, Irgolic & Meyers, 1983), and the S—P—S angle [97·45 (5)°] is similar to the corresponding S—As—S angle [96·38 (3)°]. Consequently, neither compound exhib-

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* Authors to whom correspondence should be addressed.

† Lists of structure factors, anisotropic thermal parameters and hydrogen positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52262 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses for the non*-H *atoms*

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq}
P1	0·00000	0·00000	0·39112 (5)	3·14 (3)
S1	0·04150 (6)	0·16153 (6)	0·33531 (3)	4·04 (3)
C1	−0·03887 (20)	0·21489 (19)	0·38824 (12)	3·21 (11)
C2	0·01634 (21)	0·28631 (21)	0·44724 (14)	4·02 (12)
C3	−0·04324 (25)	0·33286 (23)	0·48565 (14)	4·39 (13)
C4	−0·15774 (24)	0·30889 (22)	0·46651 (12)	4·08 (13)
C5	−0·21255 (22)	0·23721 (24)	0·40816 (14)	4·04 (12)
C6	−0·15429 (21)	0·18996 (21)	0·36894 (12)	4·9 (6)

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

P1—S1	2·122 (1)	S1—C1	1·785 (2)
C1—C2	1·385 (3)	C2—C3	1·375 (4)
C3—C4	1·374 (4)	C4—C5	1·376 (4)
C5—C6	1·377 (4)	C6—C1	1·382 (3)
S1—P1—S1	97·45 (5)	P1—S1—C1	100·03 (7)
S1—C1—C2	120·1 (2)	S1—C1—C6	120·4 (2)
C1—C2—C3	119·9 (2)	C2—C3—C4	120·8 (2)
C3—C4—C5	119·1 (2)	C4—C5—C6	121·0 (2)
C5—C6—C1	119·7 (2)	C6—C1—C2	119·5 (2)

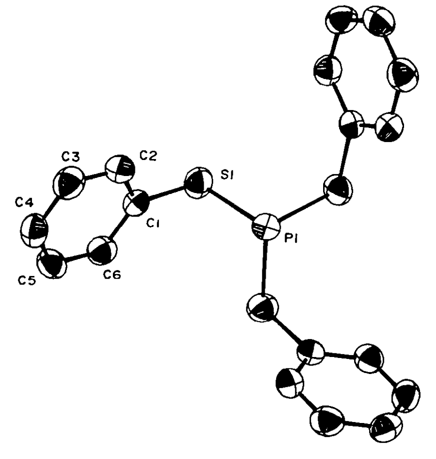

Fig. 1. *ORTEP* view of tris(phenylthio)phosphine.

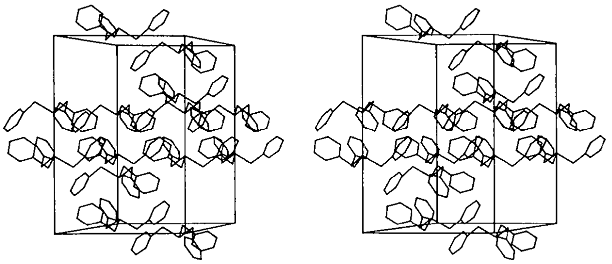

Fig. 2. Stereoview of the unit cell (*a* towards viewer, *b* vertical, *c* horizontal).

its the π structure evident in the planar nitrogen analogue $(PhS)_3N$ (Carruthers, Prout & Watkin, 1981).

The P—S bond length [2·122 (1) Å] is not significantly different from those of tris(methylthio)phosphine [2·115 (4) Å] (electron diffraction, Tuzova *et al.*, 1981), 2-chloro-1,3,2-dithiaphosphole [2·077 (15) Å] (electron diffraction, Schultz, Hargittai, Martin & Robert, 1974), 2,2-(ethylenedithio)bis(1,3,2-dithiaphosphole) [2·116 (3) Å, av.] (Newton, Brown, Finder, Robert, Martin & Tranqui, 1974) and 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole [2·106 (2) Å, av.] (Burford *et al.*, 1989). These consistent examples establish a typical P^{III}—S σ-bond distance of 2·11 Å.

While no unusual structural features are evident for the phenyl unit, the C—S bonds [1·785 (2) Å] are intermediate in length between the σ bond in $(MeS)_3P$ [1·834 (7) Å] (Tuzova *et al.*, 1981), and a π-bonded C—S bond in the 1,3,2-benzodithiaphospholium cation [1·720 (6) Å av.] (Burford *et al.*, 1989).

Conformational studies of the related tris(methylthio)phosphine have shown the presence of at least two conformers in the liquid (Fritzowsky, Lentz & Goubeau, 1971) and in the gas phase (Tuzova *et al.*, 1981), the minor of which has C_3 symmetry. In contrast, the steric constraints in the triphenyl derivative enforce the C_3 geometry in the solid state.

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Structure of Methylenecyclopropane-2-carboxamide* by Time-of-Flight Neutron Diffraction

BY ARTHUR J. SCHULTZ

Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439, *USA*

DONALD G. VAN DERVEER

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, *USA*

DAVID W. PARKER

Department of Chemistry, University of Oregon, Eugene, Oregon 97403, *USA*

AND JOHN E. BALDWIN

Department of Chemistry, Syracuse University, Syracuse, New York 13244, *USA*

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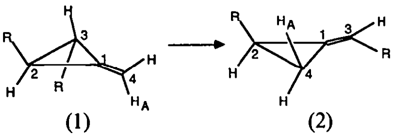
Abstract. C_5H_7NO, $M_r = 97{\cdot}1$, monoclinic, $P2_1/c$, $a = 7{\cdot}181\,(3)$, $b = 15{\cdot}495\,(5)$, $c = 8{\cdot}995\,(2)$ Å, $\beta = 104{\cdot}89\,(2)^\circ$, $V = 967{\cdot}2\,(5)$ Å^3, $Z = 8$, $D_x = 1{\cdot}33$ Mg m^{-3}, time-of-flight neutron diffraction, $\lambda = 0{\cdot}7$ to $4{\cdot}2$ Å, $\mu = 1{\cdot}98$ to $5{\cdot}90$ cm^{-1}, $T = 20$ K, $R(F) = 0{\cdot}064$, $wR(F^2) = 0{\cdot}119$ for 3150 reflections ($F_o^2 > 3\sigma$). The asymmetric unit contains two independent, but nearly identical, neutral molecules. The orientation of the exocyclic methylene group with respect to the carboxamide group is consistent with stereochemical preferences shown by methylenecyclopropane rearrangements.

Introduction. The stereochemical preferences exhibited by the [1,3] sigmatropic carbon shift in the methylenecyclopropane rearrangement, (1)→(2), a reaction that continues to attract serious theoretical scrutiny (Skancke, Schaad & Hess, 1988), are not entirely understood. A single-crystal X-ray structure determination of methylenecyclopropane-2-carboxamide revealed a displacement of the exocyclic methylene carbon C(4) toward the carboxamide-substituted ring carbon C(2), which is the preferred pivot atom in the methylenecyclopropane rearrangement (Van Derveer, Baldwin & Parker, 1987). We have undertaken a neutron diffraction investigation in order to locate precisely the hydrogen atoms and fully characterize the molecular geometry.



(1) (2)

Experimental. Time-of-flight (TOF) neutron diffraction data were obtained at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory using the single-crystal diffractometer equipped with an area position-sensitive ^{6}Li-glass scintillation detector and an Air Products Displex closed-cycle helium refrigerator for cooling the sample (Schultz, 1987). A 0·6 × 1·6 × 2·2 mm crystal, obtained by very slow concentration through evaporation of a benzene solution of the amide, was maintained at a temperature of 20 K. 24 crystal orientations were required to cover a unique quadrant of reciprocal space. For each crystal setting, data were stored in three-dimensional histogram form with coordinates x, y, t corresponding to horizontal and vertical detector positions and the TOF, respectively. The 120 TOF histogram channels were constructed with

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* IUPAC name: 2-methylenecyclopropanecarboxamide.

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