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Tris(*tert*-butyl)phosphine sulfide, a phosphine sulfide with three bulky substituents

Hans-Uwe Steinberger, Burkhard Ziemer* and Manfred Meisel

Institut für Chemie, Humboldt-Universität zu Berlin, Hessische Straße 1-2, 10115 Berlin, Germany
Correspondence e-mail: burkhard=ziemer@chemie.hu-berlin.de

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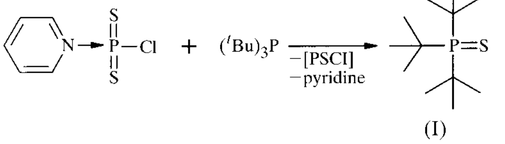
The title compound, $C_{12}H_{27}PS$, has crystallographic C_3 symmetry. The bond angles at phosphorus are tetrahedral [C—P—S 109.31 (12)° and C—P—C 109.63 (12)°] and the P—C bond length is 1.899 (4) Å. The shortest intermolecular contacts exist between methyl H atoms and the S atom (3.09, 3.12 and 3.28 Å). A survey of various phosphine sulfides containing three equal ligands (Me_3PS, Et_3PS, Cy_3PS, $^{t}Bu_3PS$, *etc.*) shows the influence of substituents with different steric demand on the geometry at phosphorus and on the P—C bond length.

Comment

Phosphine sulfides have been well known since the first reports in the early 1960's (Zingaro & Hedges, 1961; Zingaro, 1963). Subsequent studies concentrated on complex formation with transition metals and group 13 compounds (*i.e.* Ga, In; for example, $GaX_3{\cdot}2S{=}PPh_3$, where X = Cl, Br, I) (Lobana, 1992). Additionally, the formation of charge-transfer complexes from phosphine chalcogenides and diiodine in different stoichiometries [$Ph_3P{=}X{\cdot}I_2$; X = O, S, Se (Gofrey *et al.*, 1997) and $2Ph_3PS{\cdot}3I_2$ (Arca *et al.*, 1999)], and their structures have been studied.



(I)

We report here the structure of tris(*tert*-butyl)phosphine sulfide, (I), which, to the best of our knowledge, is the most sterically strained compound in this class up to now. The X-ray structure is shown in Fig. 1 and the important structural data, together with a series of comparable phosphine sulfides [Me_3PS (X-ray: Eller & Corfield, 1971; electron diffraction: Wilkins *et al.*, 1975), Ph_3PS (monoclinic: Codding & Kerr, 1978; triclinic: Ziemer *et al.*, 2000), Cy_3PS (Cy is cyclohexyl; Kerr *et al.*, 1977), *etc.*] are summarized in Table 1. In (I), the geometry at the P atom is tetrahedral within the limits of error [mean C—P—C angle 109.63 (12)°]. The corresponding average S—P—C angle is 109.31 (12)°. As can be seen from Table 1, the C—P—C angle distinctly grows from Me_3PS [105.8 (3)°] to Cy_3PS (108.0°) and (I) [109.63 (12)°] due to the increasing steric demand of the substituents at phosphorus. In spite of the low precision, the X-ray structure determination of Et_3PS (van Meerssche & Leonard, 1959) should also be mentioned [P═S 1.865 (40) Å and P—C 1.865 (40) Å; C—P—C 107° and S—P—C 112°]. The P═S bond in (I) [1.962 (3) Å], together with 1.966 (2) Å (Cy_3PS), lies at the upper limit for P═S bond distances found in phosphorus sulfides. In Table 1, it is shown that the P═S bond length only differs within a small range [1.9545 (9)/1.950 (3) Å for Ph_3PS, 1.959 (2) Å for Me_3PS, 1.962 (3) Å for (I), and 1.966 (2) Å for Cy_3PS].

On the other hand, the average S—P—C angle increases with smaller substituents from 109.31 (12)° in (I) to 110.9° in Cy_3PS and 113.2 (3)° in Me_3PS. For alkyl- and cycloalkyl-substituted phosphine sulfides, the structural effects are due to the increasing steric demand, whereas the influence of electronic effects is small and can be neglected. For Ph_3PS, however, we found that electronic effects from the electron-withdrawing phenyl groups gain more importance and influence the molecular structure. There is a correlation between the steric effect, which lengthens the P—C bond to 1.818 (2) Å [longer than 1.798 (2) Å in Me_3PS], and an electronic effect, which shortens the P═S bond to 1.9545 (9) Å, the shortest P═S distance found in the series of phosphine sulfides discussed here. Therefore, the C—P—C angle in Ph_3PS [105.6 (8)°], which is equal to 105.8 (3)° in Me_3PS, is decreased by electronic effects also. The increasing electronic effects in triphenylphosphine compounds, in comparison with alkyl phosphine compounds, are visually shown on a steric and electronic map (Tolman, 1977).

In the discussed phosphine sulfides with increasing steric demand, the P—C bond is dramatically lengthened from 1.798 (2) Å in Me_3PS (with no steric stress) to 1.899 (4) Å in

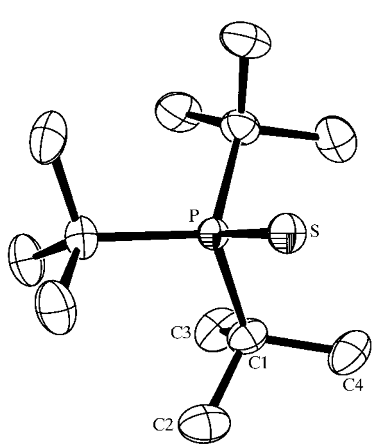


Figure 1
ORTEP-3 (Farrugia, 1997) plot of the molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms and the minor disorder component have been omitted for clarity.

(I). The comparison of the latter value with 1.798 (2) Å in Me_3PS and 1.844 (2)/1.840 (2) Å in Cy_3PS shows that there is a significant change depending on the steric demand from a primary (methyl) to a secondary (cyclohexyl) and a tertiary alkyl substituent [*tert*-butyl in (I)]. This has the effect of lengthening the P—C bond in (I) to 1.899 (4) Å, which, to the best of our knowledge, is the longest P—C bond known in the phosphine sulfide family.

tert-Butyl-2-phenylethenyl-2-phenylethynylphosphine sulfide, (II), contains an unstrained *tert*-butyl group (Mahieu *et al.*, 1997). The two unsaturated substituents are slim ligands and the P—C bond length (P—*tert*-butyl) is 1.827 (4) Å [mean P—C distance 1.791 (4) Å]. However, longer P—C bond distances, in comparison with (I), are described for tris(*tert*-butyl)phosphine [mean P—C distance 1.911 (2) Å and mean C—P—C angle 107.5 (3)°; Bruckmann & Krüger, 1995] and for the tetrakis(*tert*-butyl)phosphonium cation [1.924 (4) Å and 109.47°; Schmidbaur *et al.*, 1980].

Structural data for the complete series of tris(*tert*-butyl)phosphine chalcogenides, $^t\mathrm{Bu}_3\mathrm{P}X$ (X = O, S, Se, Te), have been summarized recently (Steinberger *et al.*, 2001). From a comparison of the corresponding P—C distances, it can be seen that there is no great difference between the shortest distance in $^t\mathrm{Bu}_3\mathrm{PO}$ [1.888 (6) Å] and the longest one in $^t\mathrm{BuPSe}$ [1.9079 (14) Å]. The C—P—C angles are also very similar and amount to about 110° (Steinberger *et al.*, 2001). Also, for $^t\mathrm{Bu}_3\mathrm{PNH}$, the corresponding data are in the same order [P—C 1.913 (6) Å and C—P—C 109.4 (5)°; Rankin *et al.*, 1985]. This indicates that in the case of the neutral $^t\mathrm{Bu}_3\mathrm{P}X$ compounds, there is no strong steric or electronic influence of the different chalcogenes and the isoelectronic NH group, respectively, on the P—C bond lengths and the C—P—C angles.

Even when $^t\mathrm{Bu}_3\mathrm{P}X$ is substituted by a proton, *i.e.* in the case of the tris(*tert*-butyl)phosphonium ion $(^t\mathrm{Bu}_3\mathrm{PH})^+$, the changes in the corresponding bond data are not very large. Thus, in the tris(*tert*-butyl)phosphonium salt of the binuclear chloroferrate(III), $(^t\mathrm{Bu}_3\mathrm{PH})_2[\mathrm{Fe}_2(\mu\text{-OEt})_2\mathrm{Cl}_6]$, slightly decreased P—C bond lengths and plausibly increased C—P—C angles were found in comparison with the neutral $^t\mathrm{Bu}_3\mathrm{P}X$ compounds [mean P—C 1.87 (1) Å and mean C—P—C 114.3 (5)°; Walker & Poli, 1990]. These results show the dominating steric influence of the bulky *tert*-butyl groups on the bonding relations in this type of compound.

In (I), the closest intermolecular distances are found between the S atom and methyl H atoms (3.09, 3.12 and 3.28 Å), which belong to three different *tert*-butyl groups. Because of the threefold symmetry around sulfur, there are nine such S···H contacts in the crystal structure. The intermolecular distances correspond to the sum of the van der Waals radii of sulfur and hydrogen (3.00 Å; Bondi, 1964). Thus, it is evident that only one hydrogen of each methyl group is directed towards the S atom.

Experimental

Tris(*tert*-butyl)phosphine sulfide was prepared during the reaction of pyridine dithiomonometaphosphoryl chloride ($\mathrm{py}\rightarrow\mathrm{PS_2Cl}$; 640 mg, 3.05 mmol; Mersel & Grunze, 1968) and tris(*tert*-butyl)phosphine (617 mg, 3.05 mmol) in benzene at room temperature. The reaction mixture was stirred overnight and a yellow solid was formed. After filtration, the solvent was completely evaporated *in vacuo* and a colourless solid was isolated (700 mg, 98% yield). Crystals suitable for X-ray analysis were obtained by recrystallization from toluene at 235 K. The compound was completely characterized. ^{31}P NMR (121.472 MHz, $CDCl_3$, 298 K): δ = 89.67 p.p.m. ($^3J_{\mathrm{P-H}}$ = 13.6 Hz); ^{1}H NMR (300.130 MHz, $CDCl_3$, 298 K): δ = 1.31 p.p.m. [*d*, $^3J_{\mathrm{H-P}}$ = 13.6 Hz, $C(CH_3)_3$]; ^{13}C NMR (75.148 MHz, $CDCl_3$, 298 K): δ = 41.40 [*d*, $^2J_{\mathrm{C-P}}$ = 34 Hz, $C(CH_3)_3$], 30.02 p.p.m. [$C(CH_3)_3$]; MS (70 eV) [*m*/*e* (%)]: 234 (8.3) [M^+], 178 (18.8) [$M^+ - C_4H_8$], 122 (36.2) [$M^+ - 2C_4H_8$], 57 (100) [$^t\mathrm{Bu}^+$], 41 (27.6) [$C_3H_5^+$].

Crystal data

$C_{12}H_{27}PS$
M_r = 234.37
Cubic, $Pa\overline{3}$
a = 14.232 (12) Å
V = 2883 (4) Å^3
Z = 8
D_x = 1.080 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
θ = 14.0–15.0°
μ = 0.30 mm^{-1}
T = 180 (2) K
Cube, colourless
0.68 × 0.60 × 0.57 mm

Data collection

Stoe Stadi-4 diffractometer
$2\theta/\omega$ scans [ratio = 0, width (ω) = 3.2°]
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.820, $T_{\max}$ = 0.846
1065 measured reflections
901 independent reflections
816 reflections with $I > 2\sigma(I)$
R_{int} = 0.009
$\theta_{\max}$ = 25.5°
$h = -12 \rightarrow 12$
$k = -1 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 1.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.136
S = 1.33
901 reflections
57 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 9.0951P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.003
$\Delta\rho_{\max}$ = 0.35 e Å^{-3}
$\Delta\rho_{\min}$ = −0.34 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0027 (5)

Table 1
Structural data (Å, °) of various phosphine sulfides.

	(I)	Me_3PS	Ph_3PS triclinic	Ph_3PS monoclinic	Cy_3PS	(II)†
P—C	1.899 (4)	1.798 (2)	1.814 (2) 1.818 (2) 1.823 (2)	1.818 (8)	1.844 (2) 1.840 (2)	1.827 (4) 1.804 (4) 1.743 (4)
P═S	1.962 (3)	1.959 (2)	1.9545 (9)	1.950 (3)	1.966 (2)	1.951 (1)
C—P—C	109.63 (12)	105.8 (3)	105.6 (8)	105.7 (6)	108.0	104.8 (6)
S—P—C	109.31 (12)	113.2 (3)	113.1 (6)	113.1 (6)	110.9	114.2 (6)

† (II) is *tert*-butyl-2-phenylethenyl-2-phenylethynylphosphine sulfide.

At the end of the usual refinement, all methyl C atoms revealed very anisotropic displacement parameters and thus two sets of split sites were introduced for these atoms. In the proceeding refinement, the set occupation ratio converged to about 70/30. Thus, R_1(gt) and wR_2(all) decreased from 0.095 and 0.196 to 0.063 and 0.136, respectively. Additionally, the deviations from the zero level in the corresponding final difference maps dropped from −0.62 and 0.71 to −0.35 and 0.34 e Å^{-3}, respectively, and the displacement ellipsoids became normal (Fig. 1). On the other hand, the P—C1 distance changed insignificantly from 1.896 (6) to 1.899 (4) Å. The H atoms were treated as riding with C—H distances of 0.98 Å.

Data collection: *STADI*4 (Stoe & Cie, 1997); cell refinement: *STADI*4; data reduction: *XRED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XSTEP* (Stoe & Cie, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1020). Services for accessing these data are described at the back of the journal.

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