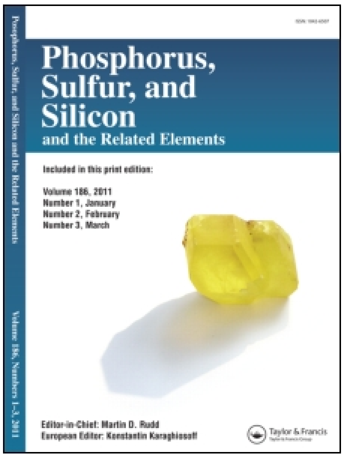

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CRYSTAL STRUCTURE OF T-BUTYL PERTHIOPHOSPHONIC ANHYDRIDE, $(t\text{-}C_4H_9PS_2)_2$, AND ITS SELENIUM ANALOG $(t\text{-}C_4H_9PSe_2)_2$

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Crystals of the title sulfur compound are orthorhombic, *Cmca*, with $a = 9.872$ (1), $b = 9.594$ (1), and $c = 15.488$ (1) Å, $V = 1467.0$ (4) Å^3, $Z = 4$, and $D_c = 1.38\,\text{g cm}^{-2}$. The final refinement using 537 observed reflections for 57 variable gave $R = 0.025$. The non-isomorphous crystals of the selenium analog are also orthorhombic, *Cmca*, with $a = 9.300$ (1), $b = 19.724$ (1), $c = 8.064$ (1) Å, $V = 1479.1$ (4) Å^3, $Z = 4$, and $D_c = 2.21\,\text{g cm}^{-2}$. Refinement with 48 variables using 447 observed reflections gives $R = 0.041$. In both structures the molecules have $2/m$ symmetry imposed by the lattice symmetry; the S (or Se) atoms of the central 4-membered ring are located on the rotation axis, and the P, exo S (or Se), and two carbon atoms of the t-butyl group lie on the mirror plane. The central rings are not readily hydrolyzed or oxidized by exposure to air, apparently as a result of steric protection provided by the t-butyl groups.

Key words: Crystal; structure; perthiophosphonic; perselenophosphonic; thionophosphine; organophosphonic.

INTRODUCTION

Thio derivatives of organophosphonic acid anhydrides, $(RPS_2)_n$, are generally considered to be dimeric with 4-membered P-S rings and trans organic groups. These molecules, which are of commercial interest in the preparation of lubricant oxidation inhibitors, are usually moisture sensitive in the solid state.[1,2] The structures of the title compounds were studied (a) to evaluate the steric factors of the t-butyl derivatives which might explain their unusual inertness to oxygen and moisture, (b) to verify their ring sizes, and (c) to determine the extent of their ring planarity. The structure of the selenium derivative apparently represents the first report of a cyclic P-Se molecule and thus allows an evaluation of the structural effects of the larger chalcogen atom in these compact rings.

RESULTS AND DISCUSSION

In the solid state the molecules of both $(t\text{-}C_4H_9PS_2)_2$ and $(t\text{-}C_4H_9PSe_2)_2$ are centered on special lattice positions of symmetry $2/m$. In each structure a 2-fold rotation axis passes through the two chalcogen atoms of the ring, and a mirror plane perpendicular to that axis includes the phosphorus atoms and the exo-cyclic atoms bonded to the phosphorus atoms; the mid-ring center of symmetry imposes a planarity to the rings and a trans arrangement of the t-butyl groups. In fact, a cis orientation of the organic groups using the central-ring distances and angles found in this study would give impossible methyl–methyl contacts of 1.2 Å. Both crystals have a lattice symmetry of *Cmca,* and although their *a* cell lengths are similar and their *b* and *c* dimensions are related by factors of approximately two, the structures are not isomorphous. The packing differences are shown most readily by the projections on the *yz* plane (Figure 2).

In the sulfur molecule the ring P-S distance is 0.200 Å longer than the exo-cyclic P═S distance, similar to the differences found for $P_2S_4(NMe_2)_2$,[3] $P_2S_4Me_2$,[4] and $P_2S_6^{-2}$.[5] The t-butyl group is bent back from the ring center as was found for $(t\text{-}C_4H_9P)_4$,[6] making the P-C-C angle to the methyl group positioned over the ring 3.7° larger than the other P-C-C angles.

The central ring of the selenium molecule is less square (ring angles of 83.5 and 96.5°) than that of the sulfur molecule (ring angles of 86.0 and 94.0°), due to the increased size of the selenium atom. In both rings the P···P cross-ring distance is approximately midway between the covalent and van der Waal's separations; the S···S and Se···Se cross-ring distances are also between covalent and van der Waal's distances, at separations of 0.4–0.5 Å less than the van der Waal's values. The increase in the P-C-C angle to the methyl group over the ring center, as described above, is also noticeable in the selenium molecule. Thus the t-butyl

TABLE I

Crystal data and details of structure determination

	$P_2S_4(C_4H_9)_2$	$P_2Se_4(C_4H_9)_2$
a. Crystal data		
Formula; FW	$P_2S_4C_8H_{18}$; 304.4	$P_2Se_4C_8H_{18}$; 492.0
Space group; number	Cmca; 64	Cmca; 64
a (Å)	9.872 (1)	9.300 (1)
b (Å)	9.594 (1)	19.724 (1)
c (Å)	15.488 (1)	8.064 (1)
V (Å^3); Z	1467.0 (4); 4	1479.1 (4); 4
Dcalc (g cm^{-3})	1.38	2.21
F000; μ (cm^{-1})	640; 8.06	928; 100.1
b. Data collection		
Radiation time (h); decay	14.0; −0.9%	13.7; −0.7%
Data range (deg θ)	2–25	2–25
Absorption correction	none	0.42–1.00
Absorption method	—	psi scans
Indices scanned: max h, k, l	11, 11, 18	11, 23, 9
Refl meas; unique refl; Rint	1360; 687; 0.08	690; 690; —
Obs refl, I > 3σ	537	447
c. Refinement		
Parameters; refl/par	57; 9.4	48; 9.3
P factor in sigma equation	0.05	0.07
R; Rw; S	0.025; 0.034; 0.97	0.041; 0.051; 1.09
Final difference map max; min	0.24 (4); −0.20 (4)	0.9 (1); −0.57 (1)
Max shift/sigma	0.01	0.01

groups are able to provide good steric protection for these compact P_2S_2 and P_2Se_2 rings, and this steric factor is likely the major factor in the increased chemical stability of these molecules compared to other organo derivatives.

EXPERIMENTAL

The title compounds were prepared by the reactions of t-$C_4H_9PCl_2$ with Li_2S_2 and Li_2Se_2, respectively. For both reactions 25 mmole of the phosphine in 50 mL of benzene were added over a period of 1 h to a suspension of 25 mmole of the lithium reagent suspended in 500 mL of benzene. After 30 m at reflux the products were obtained in 55–75% yield by precipitation with pentane followed by extraction with hot benzene. Crystallographic data were obtained with an Enraf-Nonius CAD-4 diffractomer at 293 K using 4–16 deg sec^{-1} scan rates in the $\omega - 2\Theta$ mode. Mo Kα radiation ($\lambda = 0.71073$ Å) was used with a graphite monochromator. The crystals were sealed in capillary tubes under an argon atmosphere. The unit cells were determined using 25 carefully-centered reflections with $16 > 2\Theta > 22°$. The programs used were those of the Enraf-Nonius SDP package, and the structures were solved by direct methods using MULTAN11/83. In the full matrix least squares $wt^{-1} = [\sigma^2(I) + PI^2]/4F^2$, where the P values are given on Table I. In the sulfur structure the H atoms were refined isotropically, except that the z parameter of H(31) was fixed because it oscillated in value without converging. In the selenium crystal H(31) was fixed at an idealized (C-H = 0.95 Å) position and the H thermal parameters were fixed at 1.2 × the Beq of the attached C atom. Table I also gives additional crystallographic data; Table II gives the atomic coordinates and Table III gives interatomic distances and angles. The ORTEP drawing of the sulfur molecule in Figure 1 shows the atom numbering scheme employed, and Figure 2 compares the two packing schemes as viewed down the a axis.

TABLE II

Positional and thermal parameters

Atom	x/a	y/b	z/c	Beq or B
$P_2S_4(C_4H_9)_2$				
P(1)	0.000	−0.14754 (8)	0.01918 (5)	2.95 (1)
S(1)	0.15718 (8)	0.000	0.000	3.62 (2)
S(2)	0.000	−0.30621 (9)	−0.05643 (6)	4.53 (2)
C(1)	0.000	−0.1913 (3)	0.1358 (2)	3.69 (7)
C(2)	0.1264 (3)	−0.2788 (3)	0.1527 (2)	5.58 (6)
C(3)	0.000	−0.0605 (5)	0.1900 (3)	7.9 (1)
H(21)	0.126 (3)	−0.301 (2)	0.213 (2)	5.9 (7) *
H(22)	0.118 (4)	−0.362 (3)	0.121 (2)	9.2 (9) *
H(23)	0.207 (3)	−0.231 (4)	0.132 (2)	8.2 (8) *
H(31)	0.000	−0.105 (5)	0.250	9 (1) *
H(32)	0.082 (4)	−0.015 (3)	0.178 (3)	11 (1) *
$P_2Se_4(C_4H_9)_2$				
P	0.000	0.0677 (2)	0.0877 (4)	2.25 (6)
SE(1)	0.1820 (1)	0.000	0.000	2.51 (2)
SE(2)	0.000	0.09145 (8)	0.3412 (2)	3.72 (3)
C(1)	0.000	0.1433 (7)	−0.051 (1)	2.5 (2)
C(2)	0.134 (1)	0.1852 (5)	−0.011 (1)	3.9 (2)
C(3)	0.000	0.1235 (7)	−0.232 (2)	3.1 (3)
H(21)	0.14 (1)	0.227 (5)	−0.08 (1)	4.7 *
H(22)	0.12 (1)	0.202 (5)	0.11 (1)	4.7 *
H(23)	0.21 (1)	0.154 (6)	−0.01 (1)	4.7 *
H(31)	0.000	0.163	−0.30	3.7 *
H(32)	0.083	0.097	−0.25	3.7 *

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) * [a2 * B(1, 1) + b2 * B(2, 2) + c2 * B(3, 3)].

TABLE III

Intramolecular distances (A) and angles (deg)

	$P_2S_4(C_4H_9)_2$	$P_2Se_4(C_4H_9)_2$
P–S(1)*	2.121 (1)	2.269 (2)
P–S(2)	1.921 (1)	2.097 (4)
P–C(1)	1.854 (3)	1.86 (1)
C(1)–C(2)	1.526 (4)	1.53 (1)
C(1)–C(3)	1.511 (6)	1.51 (2)
P···P′	2.893 (2)	3.022 (6)
S(1)···S(1)′	3.103 (2)	3.385 (2)
C–H (range)	0.94 (4)	0.95 (8)
	–1.02 (2)	–1.0 (1)
P–S(1)–P′	85.98 (5)	83.5 (1)
S(1)–P–S(2)	116.33 (3)	115.8 (1)
S(1)–P–S(1)′	94.02 (5)	96.5 (1)
S(2)–P–C(1)	114.5 (1)	113.9 (4)
S(1)–P–C(1)	106.71 (8)	106.5 (2)
P–C(1)–C(2)	107.0 (2)	107.9 (7)
P–C(1)–C(3)	110.7 (3)	111.9 (9)
C(2)–C(1)–C(2)′	109.6 (4)	109 (1)
C(2)–C(1)–C(3)	111.2 (3)	110.0 (7)

* For the second column, substitute the labels Se(1)/Se(2) for S(1)/S(2).

′ Atom related by $-x\ -y\ -z$ to coordinates given on Table II.

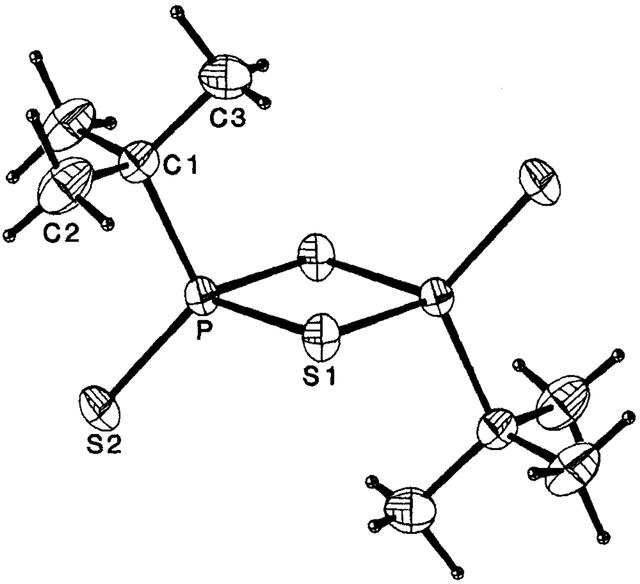

FIGURE 1 An ORTEP illustration of $P_2S_4(C_4H_9)_2$ showing the atom numbering scheme used. The thermal ellipsoids are shown at the 30% probability level and the hydrogen atoms have been given arbitrary radii.

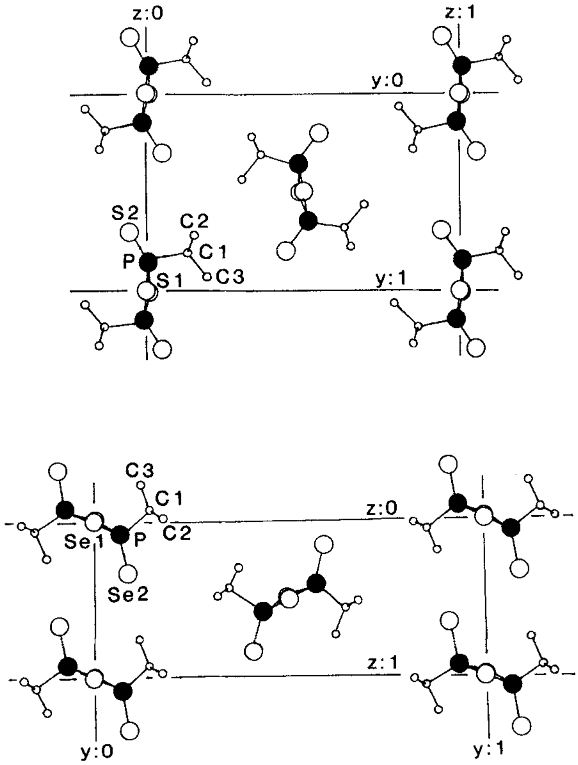

FIGURE 2 The crystal packing of $P_2S_4(C_4H_9)_2$ (above) and $P_2Se_4(C_4H_9)_2$ (below) as projected on the yz plane. The molecules shown are those centered on the mirror plane at $x = 0$. At $x = 0.5$ the layer is shifted by 0.5 in y.

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