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Tris(*O*-4-*tert*-butylphenyl)thiophosphate, C₃₀H₃₉O₃PS

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Abstract

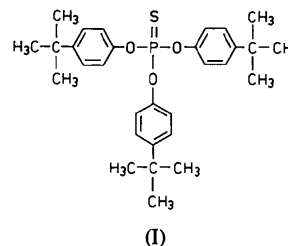
The P—O bond of the title compound is aligned along a threefold symmetry axis, making the three 4-(*tert*-butyl)phenyl groups crystallographically equivalent. The P atom is bonded to three O and one S atom, forming a distorted tetrahedron: O—P—S = 117(1), O—P—O = 100(1)°, P—S = 1.908(1), P—O = 1.579(2) Å. Neither the phenyl ring nor the attached *tert*-butyl group exhibit any unexpected geometrical features.

Comment

Some sulfur-containing organo-phosphorus compounds have received attention because of their insecticide activity (*e.g.* Schrader, 1954, 1961; Duspiva, 1954; Engelhard, Prehal & Menner, 1967). Therefore, we have synthesized a number of such compounds and investigated their chemical, thermal and spectroscopic properties (Odabaşoğlu & Gümrükçüoğlu, 1993).

The asymmetric unit of the title compound, (I), comprises one third of the formula unit; P and S are located in special positions on the threefold axis. Judged from the displacement parameters, there is no indication

of any disorder in the crystal structure; the displacement ellipsoids suggest torsional oscillation of the *tert*-butyl groups.



The geometry about the P atom corresponds to a distorted tetrahedron: the P atom is displaced from the basal plane through the crystallographically equivalent O atoms O(1), O(1ⁱ) and O(1ⁱⁱ) towards the apical atom S(1) by 0.726(2) Å [symmetry codes: (i) $-x + y, -x, z$; (ii) $-y, x - y, z$]. The O—P—S angle [117.4(1)°] is wider and the O—P—O angle [100.5(1)°] is smaller than the ideal tetrahedral angle of 109.5°.

The P=S double-bond distance [1.908(1) Å] is in the range of bond lengths reported by Schomaker & Stevenson (1941) for PSF₃ (1.85 Å) and for PSCl₃ (1.91 Å). Obviously, the electron affinities (2.8, 3.5 and 4.0 for Cl, O and F, respectively) have a distinct effect on the apical P—S bonds: the larger the electron affinity, the shorter the P—S bond. The P—O bond length [1.579(2) Å] agrees with that of the P—OH bond of orthophosphoric acid (1.576 Å; *International Tables for X-ray Crystallography*, 1983, Vol. III).

As a result of the influence of the aromatic ring, the C(4)—O(1) single bond [1.401(3) Å] is slightly

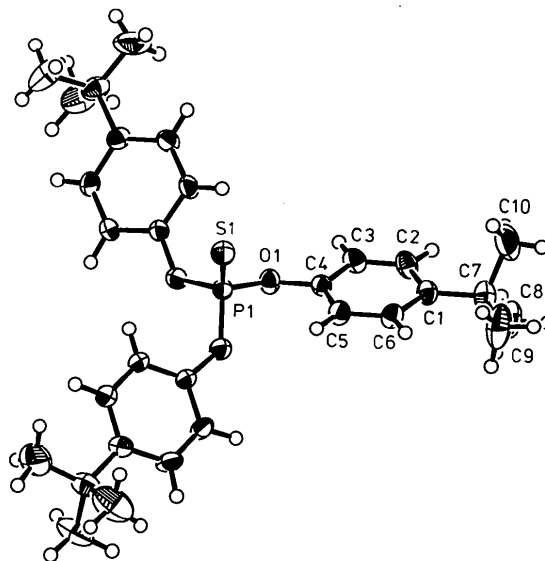


Fig. 1. Perspective view of the molecule, showing 50% probability ellipsoids. The asymmetric unit comprises one third of the molecule.

shorter than a normal paraffinic C—O bond (1.43 Å; *International Tables for X-ray Crystallography*, 1983, Vol. III).

Distances and angles within the aromatic ring are normal except for C(1)—C(2)—C(3) [122.0 (2)°], C(1)—C(6)—C(5) [121.9 (2)°] and C(2)—C(1)—C(6) [117.0 (2)°]; the values of these angles are probably a result of the steric effects of the *tert*-butyl group.

Experimental

The title compound was prepared by reaction of 4-*tert*-butylphenol with phosphorus thiochloride, PSCl₃, for 30 min at 423 K. The excess PSCl₃ was removed under reduced pressure; the remaining solid residue was purified and crystallized from *n*-hexane. Crystals suitable for X-ray diffraction were obtained by slowly cooling a saturated solution in hot PSCl₃ to room temperature.

Crystal data

C₃₀H₃₉O₃PS

M_r = 510.64

Trigonal

*R*3c (hexagonal axes)

a = 13.829 (2) Å

c = 26.687 (4) Å

V = 4419.6 (13) Å³

Z = 6

D_x = 1.151 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 4.5–15.5°

μ = 0.191 mm⁻¹

T = 233 (2) K

Plate-like

0.60 × 0.60 × 0.40 mm

Colourless, semi-transparent

Data collection

Syntex R3 diffractometer

ω scans

Absorption correction: none

15 172 measured reflections

1780 independent reflections

1644 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.028

θ_{max} = 32.5°

h = -20 → 16

k = -11 → 20

l = -40 → 40

3 standard reflections

monitored every 200

reflections

intensity decay: ≤3.7%

Refinement

Refinement on *F*²

R(*F*) = 0.044

wR(*F*²) = 0.107

S = 1.118

1780 reflections

158 parameters

w = 1/[σ²(*F*) + 0.00066*F*²]

(Δ/σ)_{max} = 0.004

Δρ_{max} = 0.40 e Å⁻³

Δρ_{min} = -0.17 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
P(1)	0	0	0.1106 (1)	0.0305 (2)
S(1)	0	0	0.1821 (1)	0.0388 (2)
O(1)	0.1169 (1)	0.0542 (1)	0.0834 (1)	0.0373 (4)
C(1)	0.3867 (2)	-0.0001 (2)	0.1040 (1)	0.0346 (5)

C(2)	0.3981 (2)	0.0973 (2)	0.0829 (1)	0.0408 (6)
C(3)	0.3084 (2)	0.1145 (2)	0.0776 (1)	0.0370 (5)
C(4)	0.2038 (2)	0.0323 (2)	0.0928 (1)	0.0305 (5)
C(5)	0.1884 (2)	-0.0649 (2)	0.1140 (1)	0.0372 (5)
C(6)	0.2803 (2)	-0.0803 (2)	0.1195 (1)	0.0369 (6)
C(7)	0.4878 (2)	-0.0164 (3)	0.1092 (1)	0.0469 (6)
C(8)	0.5384 (3)	-0.0102 (4)	0.0574 (1)	0.071 (1)
C(9)	0.4578 (4)	-0.1265 (5)	0.1347 (2)	0.089 (2)
C(10)	0.5778 (4)	0.0790 (6)	0.1414 (2)	0.086 (1)

Table 2. Selected geometric parameters (Å, °)

P(1)—S(1)	1.908 (1)	C(3)—C(4)	1.380 (3)
P(1)—O(1)	1.579 (2)	C(4)—C(5)	1.373 (3)
O(1)—C(4)	1.401 (2)	C(5)—C(6)	1.397 (3)
C(1)—C(2)	1.393 (3)	C(7)—C(8)	1.533 (4)
C(1)—C(6)	1.390 (3)	C(7)—C(9)	1.524 (5)
C(1)—C(7)	1.529 (3)	C(7)—C(10)	1.545 (5)
C(2)—C(3)	1.383 (3)		
O(1)—P(1)—O(1)	100.53 (8)	C(3)—C(4)—O(1)	115.4 (2)
S(1)—P(1)—O(1)	117.38 (7)	C(4)—C(5)—C(6)	118.9 (2)
P(1)—O(1)—C(4)	127.0 (1)	C(1)—C(6)—C(5)	121.9 (2)
C(6)—C(1)—C(2)	117.0 (2)	C(9)—C(7)—C(1)	112.1 (2)
C(6)—C(1)—C(7)	122.5 (2)	C(9)—C(7)—C(8)	110.4 (3)
C(2)—C(1)—C(7)	120.6 (2)	C(1)—C(7)—C(8)	109.6 (2)
C(3)—C(2)—C(1)	122.0 (2)	C(9)—C(7)—C(10)	107.7 (4)
C(4)—C(3)—C(2)	119.3 (2)	C(1)—C(7)—C(10)	109.3 (3)
C(5)—C(4)—C(3)	120.9 (2)	C(8)—C(7)—C(10)	107.6 (3)
C(5)—C(4)—O(1)	123.7 (2)		

Data collection used a variable scan speed of 4–12° min⁻¹, a scan width from 0.8° below *K*₁ to 0.8° above *K*₂ and a background/scan ratio of 0.5. Intensities were corrected for Lorentz-polarization effects, but not for absorption. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985, 1990) and refined by full-matrix least-squares using *SHELXL93* (Sheldrick, 1993). H atoms were located by difference Fourier methods; the methyl H atoms were initially constrained to an ideal geometry (C—H bond length 0.96 Å). All H atoms were included in the final refinement cycles with isotropic displacement factors. Intensity statistics strongly suggest the absence of a centre of symmetry; the Flack (1983) absolute structure parameter [0.04 (13)] supports our choice of polarity. Polar-axis restraints were applied by the method of Flack & Schwarzenbach (1988) in order to fix the origin along the polar axis. Molecular graphics were produced using *ORTEP* (Johnson, 1965).

The diffractometer data were collected at the Institut für Kristallographie der Universität Karlsruhe. We are indebted to Prof. Dr D. Fenske, Institut für Anorganische Chemie der Universität Karlsruhe, for providing computing facilities.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: SH1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,1-Dichloro-3,3,5,5-tetraphenyl- $1\lambda^4,2,6,3\lambda^5,5\lambda^5$ -selenadiazadiphosporin

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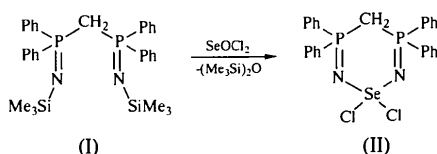
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Abstract

The first X-ray structure of a six-membered ring containing the structural unit N—SeCl₂—N is presented. The heterocycle in the title compound (as the trichloromethane solvate), C₂₅H₂₂Cl₂N₂P₂Se·2CHCl₃, adopts a boat conformation with the C and Se atoms deviating from the P₂N₂ plane. The two Se—Cl bonds differ markedly. Disorder of one of the phenyl groups may be explained in terms of the crystal packing.

Comment

The reaction leading to the title compound presents a new method for the synthesis of cyclic metallophosphazenes (Seseke, 1986). The reaction of (I) with WF₆ and WCl₆ yields analogous products which have been characterized by NMR spectroscopy. Compounds of type (I) with one, two and three methylene groups bridging the two P atoms have been investigated by Appel & Ruppert (1974), who showed the possibility of transforming (I) into cyclic products.



The title compound, (II), crystallizes with two chloroform molecules in the asymmetric unit. The heterocycle adopts a boat conformation with Se and C(1) deviating [by 0.32 (1) and 0.64 (1) Å, respectively] from the P₂N₂ plane ($\sigma = 0.023$ Å).

Taking into account the free electron pair, the Se coordination geometry can be described as trigonal bipyramidal with the lone pair and the two N atoms in the equatorial plane, while the Cl atoms occupy the axial positions. The Se—N bond lengths are shortened compared with an Se—N single bond. The two Se—Cl bonds differ by nearly 0.5 Å. Both P=N double bonds display typical values. The phenyl rings C11—C16 and C21—C26 are approximately parallel, the angle between them being 19.7 (6)°.

Inspection of the crystal packing reveals that the disordered phenyl ring is surrounded by other disordered phenyl rings and chloroform molecules, while the ring C11'—C16' lies in the vicinity of the nearly parallel aromatic rings which restrict its degrees of freedom. Therefore, it seems obvious that the crystal packing allows different orientations of one phenyl group while keeping the other in a more fixed position.

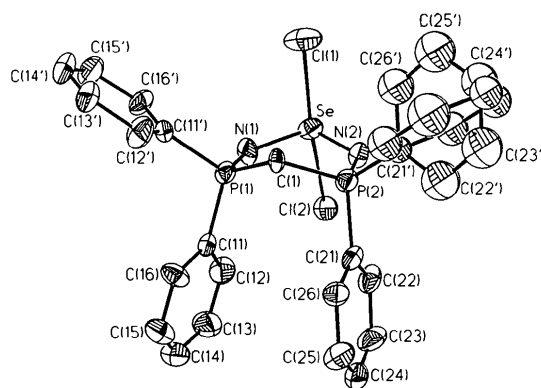


Fig. 1. View of C₂₅H₂₂Cl₂N₂P₂Se·2CHCl₃ showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 30% probability level.

Experimental

Crystal data

C₂₅H₂₂Cl₂N₂P₂Se·
2CHCl₃
M_r = 800.98
Monoclinic
P2₁/n
a = 10.785 (5) Å
b = 15.709 (6) Å
c = 20.884 (8) Å
β = 100.89 (3)°
V = 3474.5 (9) Å³
Z = 4
D_x = 1.531 Mg m⁻³

Mo Kα radiation
λ = 0.71069 Å
Cell parameters from 40
reflections
θ = 10–12.5°
μ = 1.810 mm⁻¹
T = 293 K
Transparent block
0.70 × 0.30 × 0.30 mm
Yellow
Crystal source: dimethyl-
formamide/chloroform