

***O,O*-Bis(2-*tert*-butyl-4-methylphenyl)
chlorothiophosphonate**Mustafa Odabaşođlu,^{a*} Orhan
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Key indicators

Single-crystal X-ray study

 $T = 296\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.012\text{ \AA}$ R factor = 0.035 wR factor = 0.090

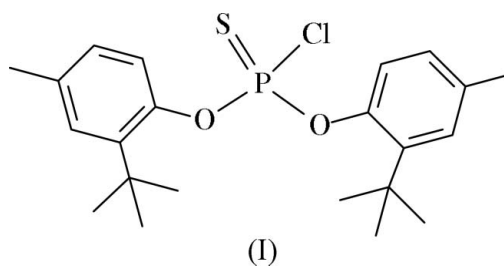
Data-to-parameter ratio = 16.9

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{22}\text{H}_{30}\text{ClO}_2\text{PS}$, displays distorted tetrahedral geometry around the P atom. The dihedral angle between the benzene rings is $43.7(4)^\circ$. The aromatic rings have unusual endocyclic angles as a result of the steric effects of the *tert*-butyl groups. The molecules are linked by weak $\text{C}-\text{H}\cdots\pi$ interactions.

Comment

The conformational study of phosphoric acid esters has been mainly encouraged by the behaviour exhibited by these compounds in biological systems. In addition, owing to their biological activities and increasing industrial use in food manufacture and water treatment, and as antioxidants, anti-corrosives, insecticides, detergents, oil additives, heavy metal ion-selective electrodes, ligands and resins, thiophosphorus compounds have attracted considerable attention (Bellamy & Beecher, 1952; Schrader, 1954; Corbridge, 1956; Engelhard *et al.*, 1967; Pastor *et al.*, 1988; Odabaşođlu & Gümrükçüođlu, 1993; Mastrantonio & Della Vedova, 2001; Xu & Katsu, 2001; Ibrahim *et al.*, 2003). In the course of a systematic structural investigation of thiophosphorus compounds (Odabaşođlu *et al.*, 1999; Yılmaz *et al.*, 1998; Büyükgüngör *et al.*, 1995; Odabaşođlu & Gümrükçüođlu, 1993; Odabaşođlu *et al.*, 1992), the structure of the title compound, (I), was determined.



An *ORTEP*-3 (Farrugia, 1997) view of the molecule of (I) and a packing diagram are shown in Figs. 1 and 2, respectively. Compound (I) exhibits no classical hydrogen bonds but does exhibit $\text{C}-\text{H}\cdots\pi$ contacts: $\text{H}31\text{A}\cdots\text{Cg}1 = 2.583\text{ \AA}$, $\text{C}31\cdots\text{Cg}1 = 3.483(10)\text{ \AA}$ and $\text{C}31-\text{H}31\text{A}\cdots\text{Cg}1 = 156^\circ$ [$\text{Cg}1$ is the centroid of the $\text{Cl}^1-\text{C}6^1$ ring; symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$]. The dihedral angle between the benzene rings in (I) is $43.7(4)^\circ$. Selected bond distances and angles for (I) are given in Table 1. The endocyclic angles of the benzene rings are unusual; the diversity of the angles is probably due to steric effects of the *tert*-butyl groups.

The geometry about the P atom corresponds to a distorted tetrahedron, with the $\text{O}-\text{P}-\text{O}$ angles smaller than the ideal tetrahedral angle of 109.5° . The $\text{P}=\text{S}$ double bond distance is

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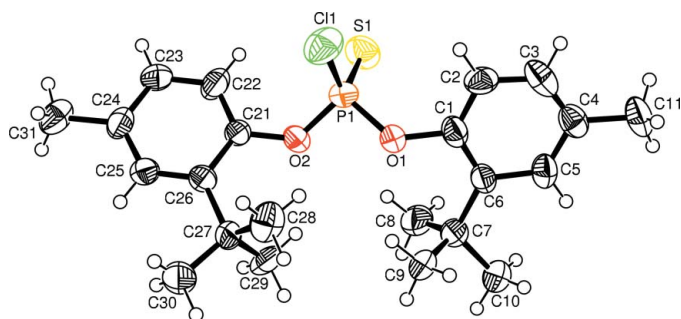


Figure 1
A view of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

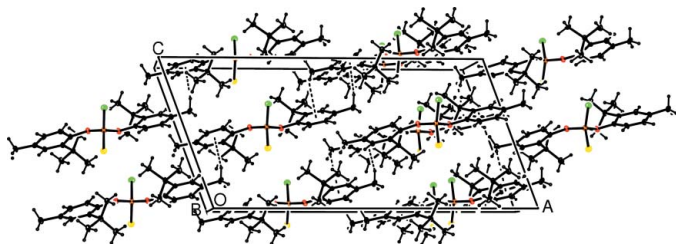


Figure 2
A view of the packing diagram for (I); C—H... π interactions are drawn as dashed lines.

in the range of bond lengths reported by Schomaker & Stevenson (1941) for PSF_3 (1.85 Å) and PSCl_3 (1.91 Å). The P—O bond lengths agree with that of the P—OH bond of orthophosphoric acid (1.576 Å; *International Tables for X-ray Crystallography*, 1983, Vol. III) and also those of our previous studies (Yılmaz *et al.*, 1998; Büyükgüngör *et al.*, 1995; Odabaşoğlu *et al.*, 1992).

Experimental

Compound (I) was prepared by the method described by Odabaşoğlu & Gümrükçüoğlu (1993) as follows. In one preparative experiment, phosphorus thiochloride (3.39 g, 0.02 mol) was added to 2-*tert*-butyl-4-methylphenol (8.2 g, 0.05 mol) in a double-necked flask kept in an oil bath; the mixture was stirred continuously at 393 K and refluxed at 323 K for 24 h. The excess phosphorus thiochloride was removed under reduced pressure, giving a white solid residue. Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in *n*-hexane (yield 57%, m.p. 401 K). Analysis calculated: C 62.19, H 7.06%; found: C 61.88, H 6.96%.

Crystal data

$\text{C}_{22}\text{H}_{30}\text{ClO}_2\text{PS}$
 $M_r = 424.94$
Monoclinic, C_c
 $a = 24.139$ (2) Å
 $b = 8.3588$ (6) Å
 $c = 11.8747$ (12) Å
 $\beta = 110.014$ (8)°
 $V = 2251.3$ (4) Å³
 $Z = 4$

$D_x = 1.254$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 7293 reflections
 $\theta = 1.8$ – 26.9 °
 $\mu = 0.35$ mm⁻¹
 $T = 296$ K
Prism, colourless
 $0.25 \times 0.23 \times 0.20$ mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
Absorption correction: by integration (*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.937$, $T_{\max} = 0.961$
14829 measured reflections

4235 independent reflections
2583 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$
 $\theta_{\max} = 26.0$ °
 $h = -29 \rightarrow 29$
 $k = -10 \rightarrow 10$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.090$
 $S = 0.86$
4235 reflections
251 parameters
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0477P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.14$ e Å⁻³
 $\Delta\rho_{\min} = -0.21$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0048 (4)
Absolute structure: Flack (1983),
with 2019 Friedel pairs
Flack parameter = 0.39 (16)

Table 1

Selected geometric parameters (Å, °).

C1—C6	1.350 (10)	C21—C26	1.426 (9)
C1—C2	1.410 (11)	C22—C23	1.406 (11)
C1—O1	1.444 (9)	C23—C24	1.425 (11)
C2—C3	1.385 (11)	C24—C25	1.390 (11)
C3—C4	1.315 (12)	C25—C26	1.357 (10)
C4—C5	1.379 (12)	O1—P1	1.576 (6)
C5—C6	1.437 (10)	O2—P1	1.545 (6)
C21—C22	1.336 (11)	P1—Cl1	1.941 (4)
C21—O2	1.385 (9)	P1—S1	1.957 (4)
C6—C1—C2	125.0 (7)	C25—C24—C23	119.1 (7)
C6—C1—O1	116.0 (7)	C26—C25—C24	123.4 (7)
C2—C1—O1	118.3 (7)	C25—C26—C21	116.9 (7)
C4—C3—C2	125.7 (8)	C21—O2—P1	129.4 (5)
C3—C4—C5	115.8 (8)	O2—P1—O1	96.81 (8)
C4—C5—C6	125.1 (8)	O2—P1—Cl1	110.8 (3)
C1—C6—C5	113.0 (7)	O1—P1—Cl1	110.5 (3)
C22—C21—O2	120.6 (6)	O2—P1—S1	111.9 (3)
C22—C21—C26	121.1 (7)	O1—P1—S1	111.1 (3)
O2—C21—C26	118.3 (6)	Cl1—P1—S1	114.41 (4)
C22—C23—C24	116.7 (7)		

All H atoms were refined using a riding model, with C—H = 0.93 Å [$U_{\text{iso}} = 1.2U_{\text{eq}}(\text{parent atom})$] for aromatic H atoms and C—H = 0.96 Å [$U_{\text{iso}} = 1.5U_{\text{eq}}(\text{parent atom})$] for methyl H atoms. The value of the Flack (1983) parameter indicates partial inversion twinning.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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