3-(3-Chloro-4-fluorophenyl)-2-(2-chlorophenoxy)-3,4-dihydro-2H-1,3,2-benzoxazaphosphorine 2-oxide

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3-(3-Chloro-4-fluorophenyl)-2-(2-chlorophenoxy)-3,4-dihydro-2H-1,3,2-benzoxazaphosphorine 2-oxide

In the title compound, C_{33}H_{21}Cl_{3}FNO_3P, the six-membered 1,3,2-oxazaphosphorine ring adopts a screw boat conformation, with the phosphoryl O atom in an axial position. The chlorofluorobenzene and chlorophenoxy groups are nearly perpendicular to each other, with a dihedral angle of 82.53 (1)$^\circ$ between them, and are equatorially oriented with dihedral angles of 59.03 (1) and 26.15 (2)$^\circ$, respectively, with respect to the mean plane of the heterocyclic ring.

Comment

The oxazaphosphorine ring system has recently attracted considerable attention because of its presence in antitumour agents (Stec, 1980). The title compound, (I), was prepared and found to possess significant antimicrobial and insecticidal activity (Kiran et al., 2005). Because of this activity, the X-ray crystal structure of (I) is of great interest to our continuing investigation of heterocyclic phosphorus compounds and is reported here (Fig. 1).

![Chemical structure of (I)]

The oxazaphosphorine ring of (I) adopts a screw boat conformation, with atoms O4, C12, C17 and C18 coplanar and atoms P1 and N5 displaced away from this plane in the same direction by 0.187 (1) and 0.750 (3) Å, respectively. The phosphoryl atom O2 occupies an axial position and atom O3 an equatorial position on the phosphorin ring. The conformation of the phosphorin ring is influenced by the steric interaction between the phosphoryl atom O2 and the chlorofluorobenzene ring. The O2...C20 distance is 3.072 (4) Å and the aromatic ring is rotated such that the angle between the C12/C17/C18/O4 and chlorofluorobenzene planes is 59.03 (1)$^\circ$.

The P-O distance of 1.446 (2) Å and the endo- and exocyclic distances and angles for the oxazaphosphorin unit are consistent with the literature values (Nutti et al., 1988; Subramanian et al., 1989; Selladurai & Subramanian, 1990,
1992; Selladurai et al., 1991; Angelov et al., 2002). The C—F [1.360 (4) Å] and average C—Cl [1.729 (3) Å] bond lengths are in good agreement with the values reported by Allen et al. (1987).

The chloro[1.729 (3) Å] and phenonxy groups are in equatorial positions on the phosphinine ring. These ring planes are perpendicular to each other [dihedral angle 82.53 (1)°] and make dihedral angles of 26.15 (2) and 59.03 (1)°, respectively, with the C12/C17/C18/O4 plane.

In the crystal structure of (I), C15—H15⋯O2 Hydrogen bonds link the molecules into chains along b, while C24—H24⋯O2 interactions form an additional, approximately orthogonal, set of chains along a (Fig. 2; symmetry codes as in Table 1).

**Experimental**

A solution of 2-chlorophenylphosphorodichloride (0.02 mol) in dry toluene (10 ml) was added dropwise to a stirred solution of 2-(3-chloro-4-fluorophenylamino)methylphenol (0.02 mol), triethylamine (0.04 mol) and a catalytic amount of dimethylaminopyridine dissolved in dry toluene (20 ml) at 273 K over a period of 20 min. After completion of the addition, the reaction temperature was slowly raised to 323–328 K and maintained at this temperature for 6–7 h. On separation of the triethylamine hydrochloride by filtration, and evaporation of the filtrate under reduced pressure, a solid residue was obtained. This was washed with water and recrystallized from chloroform to afford yellowish transparent single crystals of (I) suitable for X-ray diffraction.

**Crystal data**

C70H63Cl5FNO8P

(V = 1847.7 (8) Å³)

Z = 4

Monoclinic, P2₁/n

Mo Kα radiation

a = 6.731 (2) Å

μ = 0.47 mm⁻¹

b = 18.652 (3) Å

T = 293 (2) K

c = 15.045 (3) Å

0.30 × 0.25 × 0.14 mm

β = 101.98 (3)°

**Data collection**

Siemens SMART CCD area-
detector diffractometer

4357 measured reflections

3221 independent reflections

2887 reflections with I > 2σ(I)

R_{int} = 0.039

**Refinement**

R[F² > 2σ(F²)] = 0.060

wR(F²) = 0.170

S = 1.09

3221 reflections

Δρ_{min} = 0.73 e Å⁻³

Δρ_{max} = −0.66 e Å⁻³

Table 1

<table>
<thead>
<tr>
<th>D—H⋯A</th>
<th>D—H</th>
<th>H⋯A</th>
<th>D⋯A</th>
<th>D—H⋯A</th>
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<tr>
<td>C24—H24⋯O2'</td>
<td>0.93</td>
<td>2.36</td>
<td>3.20 (4)</td>
<td>151</td>
</tr>
<tr>
<td>C15—H15⋯O2</td>
<td>0.93</td>
<td>2.65</td>
<td>3.43 (4)</td>
<td>143</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x + 1, y, z; (ii) −x−½, y+½, z+1/2.

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H and C—H = 0.97 Å and U_{iso}(H) = 1.5U_{eq}(C) for CH₂ groups.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXL97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ZORTEP II (Zsolnai, 1998); software used to prepare material for publication: enCIFer (Allen et al., 2004) and PARST (Nardelli, 1995).

**References**


