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Key indicators

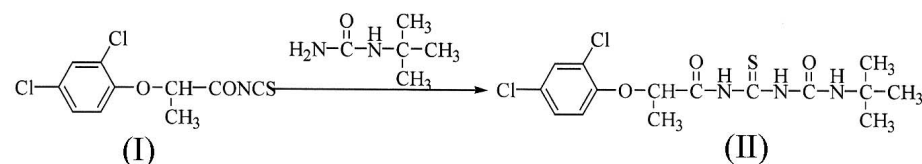
Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
 R factor = 0.080
 wR factor = 0.248
Data-to-parameter ratio = 15.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.5-*tert*-Butyl-1-[2-(2,4-dichlorophenoxy)-
propionyl]thiobiuretThe title compound, $\text{C}_{15}\text{H}_{19}\text{Cl}_2\text{N}_3\text{O}_3\text{S}$, is a phenoxythiourea compound with a *tert*-butylaminocarbonyl group attached to the distal N atom of the thiourea bridge. There are intramolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, forming six- and five-membered rings.

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Comment

Thiourea derivatives show high biological activities as agrochemicals and are used extensively as herbicides, pesticides and fungicides (Yonova & Stoilkova, 2005; Pu *et al.*, 1994; McCourt *et al.*, 2005). Compared to urea herbicides, some thiourea herbicides show high herbicidal activities; these are absorbed easily by weeds owing to the presence of a $\text{C}=\text{S}$ double bond in the molecule. Nowadays, work on thioureas as herbicides is a subject of intensive research and many novel structural thiourea herbicides have appeared in the literature (Josef, 1988; Ehrenfreund 1988; Takematsu & Suzuki, 1988; Kehne *et al.*, 1991). Recently, we have developed a phenoxythiourea with a substituted pyrimidine ring attached to the distal N atom of the thiourea bridge, which offered high herbicidal activity (Xue *et al.*, 2000). In order to research further the herbicidal effect, we have synthesized the title compound, (II), in which the pyrimidine ring is replaced by the *tert*-butylaminocarbonyl group. Changing the group attached to the distal N atom of the phenoxythiourea bridge might provide an opportunity to study the cooperative effect between the two types of biologically active groups in herbicidal applications.



The title compound consists of a 2,4-dichlorophenoxypropionyl group, a *tert*-butylaminocarbonyl group and a thiourea bridge (Fig. 1). The $\text{S}-\text{C}$ distance and $\text{N}-\text{C}-\text{N}$ angle (Table 1) are similar to those of 2-chlorobenzoyl-3-(4-methylphenyl)thiourea [$\text{S}-\text{C} = 1.660(2)\text{ \AA}$ and $\text{N}-\text{C}-\text{N} = 114.7(15)^\circ$; Li *et al.*, 2000]. A similar structure is also observed in *N'*-[2-(4-chloro-6-methoxypyrimidyl)-*N*]-[2-(2,4-dichlorophenoxypropionyl)]thiourea (Liu *et al.*, 2006). The $\text{C}-\text{O}$ and $\text{C}-\text{N}$ distances of the two CONH groups (Table 1) are in the expected range. There are intramolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, forming six- and five-membered rings (Table 2).

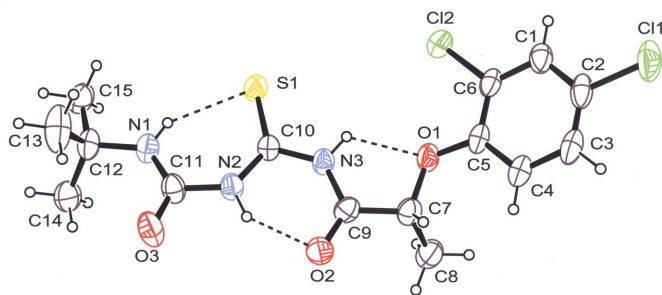


Figure 1

The molecular structure of (II), showing displacement ellipsoids at the 30% probability level and the atom-numbering scheme. Hydrogen bonds are shown as dashed lines.

Experimental

Compound (II) was synthesized using the reported method (Jiang *et al.*, 2000; Wang & Xue, 2001). The synthetic route is outlined in the scheme. To a stirred solution of (I) (0.50 g, 1.82 mmol) in acetonitrile (10 ml) was slowly added a solution of *tert*-butylaminoformamide (0.21 g, 1.82 mmol) in dry acetonitrile (10 ml) over a period of 30 min at room temperature under nitrogen. The mixture was refluxed and stirred for two h. After evaporation of most of the solvent, the residue was cooled to room temperature and water (5 ml) was added to quench the reaction. The residue was then repeatedly extracted with 50 ml of diethyl ether. The combined organic layer was washed with water and brine, and then dried over Na_2SO_4 . After evaporation of the solvent, the residue was further purified by column chromatography on silica gel (hexane/ethyl acetate, *v/v* 1:2) to give (II) (0.54 g, 1.38 mmol) as a yellow crystalline material in 76% yield. Single crystals suitable for X-ray diffraction were obtained by cooling a hot water/ethanol (*v/v* 1:9) solution to room temperature.

Crystal data

$\text{C}_{15}\text{H}_{19}\text{Cl}_2\text{N}_3\text{O}_3\text{S}$	$V = 951.1 (6) \text{ \AA}^3$
$M_r = 392.29$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.370 \text{ Mg m}^{-3}$
$a = 8.024 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.361 (3) \text{ \AA}$	$\mu = 0.47 \text{ mm}^{-1}$
$c = 12.729 (4) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 67.849 (4)^\circ$	Block, yellow
$\beta = 76.511 (4)^\circ$	$0.15 \times 0.10 \times 0.10 \text{ mm}$
$\gamma = 81.571 (5)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	3974 measured reflections
φ and ω scans	3279 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 1998)	2217 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.945$, $T_{\max} = 0.954$	$R_{\text{int}} = 0.041$
	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1522P)^2 + 0.3929P]$
$R[F^2 > 2\sigma(F^2)] = 0.080$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.248$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
3279 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$
217 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.009 (1)

Table 1

Selected geometric parameters (\AA , $^\circ$).

C11—C2	1.750 (6)	O1—C5	1.366 (6)
C12—C6	1.743 (5)	O1—C7	1.421 (6)
N1—C12	1.461 (7)	O2—C9	1.224 (6)
N2—C11	1.408 (6)	O3—C11	1.225 (7)
N3—C9	1.371 (6)	S1—C10	1.655 (5)
C11—N1—C12	125.7 (5)	O1—C7—C9	107.5 (4)
C10—N2—C11	132.6 (4)	N3—C9—C7	116.2 (4)
C9—N3—C10	130.4 (4)	N2—C10—N3	114.7 (4)
C5—O1—C7	120.3 (4)	N1—C11—N2	118.8 (5)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots S1	0.86	2.33	3.060 (5)	142
N2—H2A \cdots O2	0.86	1.96	2.686 (6)	142
N3—H3A \cdots O1	0.86	2.08	2.549 (5)	114

H atoms were positioned geometrically ($\text{C—H} = 0.93\text{--}0.98 \text{ \AA}$ and $\text{N—H} = 0.86 \text{ \AA}$) and refined using the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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