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N′-(4-Chloro-6-methoxypyrimidin-2-yl)-*N*-[2-(2,4-dichlorophenoxy)propionyl]thiourea

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Key indicators

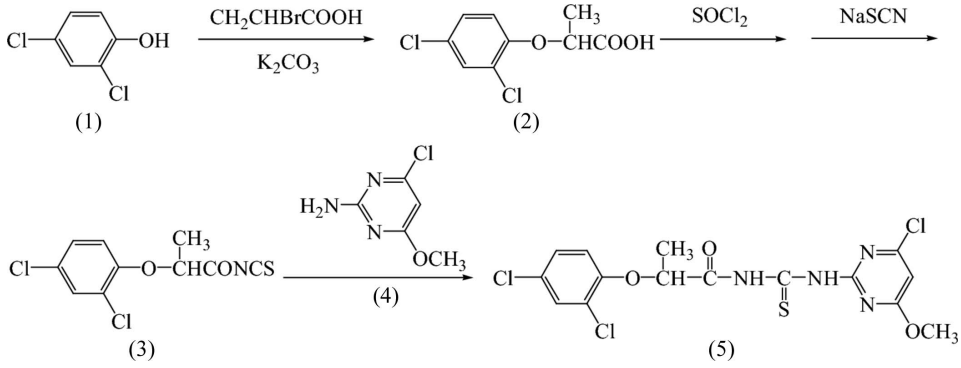
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.052
wR factor = 0.139
Data-to-parameter ratio = 14.0

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

The title compound, $C_{15}H_{13}C_{l3}N_4O_3S$, is one of the thiourea herbicides with a pyrimidine ring attached to the distal N atom of the bridge of the thiourea. The crystal structure determination reveals that intramolecular N—H···O hydrogen bonds form a six-membered and a five-membered ring, which indicates the coordination behavior of this potentially multidentate compound.

Comment

Thiourea compounds display high biological activities as herbicides with low toxicity and low residue content, and are used extensively as pesticides, fungicides and regulating agents of plant growth in the agrochemical industry (Pu *et al.*, 1994; McCourt *et al.*, 2005). Due to the low toxicity to mammals, birds, fish, amphibians *etc.*, work on thiourea derivatives as herbicides is a subject of intensive research and many novel structural thiourea herbicides have appeared in the literature (Ehrenfreund 1988; Takematsu *et al.*, 1988; Kehne *et al.*, 1991). Although some phenoxythioureas have been described (Xue *et al.*, 2000), so far, relatively few reports on crystal structures employing thioureas with a pyrimidine ring attached to the distal N atom are available (Xue *et al.*, 2005). We have developed the synthesis of (5) and report here the crystal structure of the title compound. The key feature of this phenoxythiourea is that the 2,4-dichlorophenoxypropionyl group is linked to the thiourea bridge by an amido bond and the pyrimidine ring substituted in both *meta* positions is attached to the distal N atom of thiourea, which might provide an opportunity for the study of the cooperative effect of combining these biologically active components in a single molecule.



A single-crystal X-ray structure determination (Fig. 1) shows that, in the molecular structure of (5), the phenoxypropionyl group and the pyrimidine ring are almost coplanar. The configuration of (5) with S1—C10 = 1.637 (3) Å and an

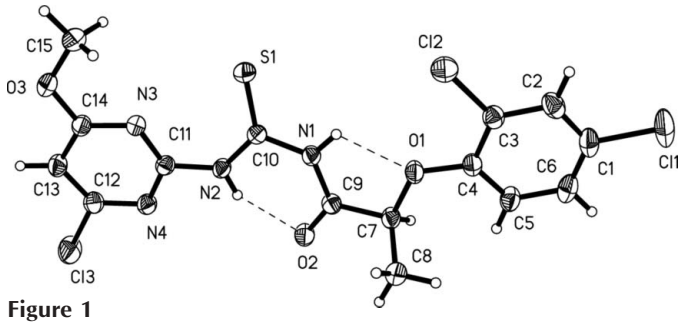


Figure 1
The structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. Hydrogen bonds are shown as dashed lines.

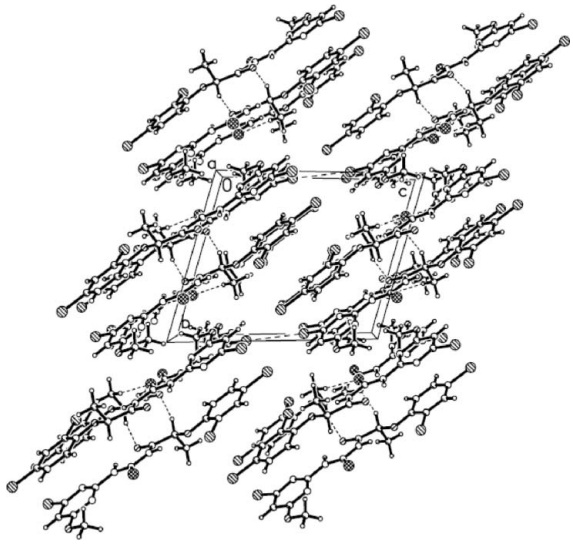


Figure 2
Perspective view of the molecular packing of the title compound, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

N2—C10—S1 angle of 129.5 (2)° is similar to that of 2-chlorobenzoyl-3-(4-methylphenyl)thiourea with S1—C8 = 1.660 (2) Å and an N1—C8—S1 angle of 126.36 (13)° reported by Li *et al.* (2000). In comparison with this compound, the C—O and C—N distance of the CONH bond [O2—C9 = 1.225 (3) Å *versus* O—C10 = 1.220 (2) Å and N1—C9 = 1.364 (4) Å *versus* N2—C10 = 1.357 (2) Å] are in the expected ranges (Table 1). There are intramolecular N—H···O hydrogen bonds, forming a six-membered ring and a five-membered ring (Table 2), which indicates the coordination behavior of these potentially multidentate systems. Zhang, Dago and co-workers (Zhang *et al.*, 1996; Cao *et al.*, 1996; Dago *et al.*, 1989) also observed similar intramolecular hydrogen-bonding patterns in the molecular structure of benzoylthioureas.

Experimental

2,4-Dichlorophenoxypropionic acid and its isothiocyanate derivative were synthesized by using the reported method (Jiang *et al.*, 2000; Wang *et al.*, 2001). The synthetic routes are indicated in the scheme. Reaction of the isothiocyanate derivative with 4-chloro-6-methoxy-2-aminopyrimidine was successfully carried out using acetonitrile as solvent as follows. To a stirred solution of (3) (0.50 g, 1.81 mmol) in acetonitrile (10 ml) was slowly added a solution of 4-chloro-6-methoxy-2-aminopyrimidine (0.29 g, 0.81 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. Then the residue was 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 crystallized from a solution of DMF/C_2H_5OH/H_2O (1:5:1 *v*/*v*/*v*) to give (5) as yellow crystals in 53% yield.

Crystal data

$C_{15}H_{13}Cl_3N_4O_3S$
M_r = 435.70
Triclinic, $P\overline{1}$
a = 7.939 (5) Å
b = 10.183 (7) Å
c = 12.764 (9) Å
α = 105.302 (10)°
β = 105.729 (9)°
γ = 90.698 (11)°
V = 954.1 (11) Å^3
Z = 2
D_x = 1.517 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 763 reflections
θ = 5.2–54.0°
μ = 0.61 mm^{-1}
T = 298 (2) K
Plate, yellow
0.15 × 0.15 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.914, T_{max} = 0.970
3986 measured reflections
3289 independent reflections
2056 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 25.0°
$h = -9 \rightarrow 8$
$k = -8 \rightarrow 12$
$l = -15 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.139
S = 0.92
3289 reflections
235 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C9	1.364 (4)	O2—C9	1.225 (3)
N1—C10	1.398 (4)	S1—C10	1.637 (3)
N2—C10	1.358 (4)		
C9—N1—C10	130.5 (3)	N2—C10—N1	112.5 (3)
O1—C7—C9	106.9 (2)	N2—C10—S1	129.5 (2)
N1—C9—C7	116.2 (3)	N1—C10—S1	118.0 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*C*···N2^{i}	0.96	2.96	3.688 (5)	134
C8—H8*C*···O3^{i}	0.96	2.67	3.435 (5)	138
C8—H8*B*···S1^{ii}	0.96	2.89	3.837 (4)	171
C7—H7*A*···S1^{iii}	0.98	2.96	3.545 (4)	120
C7—H7*A*···O2^{iv}	0.98	2.40	3.281 (4)	150
N2—H2*B*···O2	0.86	1.93	2.657 (3)	141
N1—H1*A*···O1	0.86	2.06	2.533 (3)	114

Symmetry codes: (i) $-x+2, -y+2, -z$; (ii) $x-1, y, z$; (iii) $-x+2, -y+1, -z$; (iv) $-x+1, -y+1, -z$.

H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and refined using the riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); 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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References

Bruker (1998). *SMART*, *SAINT*, *SHELXTL* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cao, Y., Zhao, B., Zhang, Y.-Q. & Zhang, D.-C. (1996). *Acta Cryst.* C**52**, 1772–1774.

Dago, A., Shepelev, Y., Fajardo, F., Alvarez, F. & Pomś, R. (1989). *Acta Cryst.* C**45**, 1192–1194.

Ehrenfreund, J. (1988). HU Patent A01N47/30, 46839.

Jiang, M. G., Yang, H., Cheng, R. D., Liu, Y. P., Bo, L. Y., Lou, Y. L., Zhang, S. M. & Zhang, D. Y. (2000). *J. Nanjing Agric. Univ.* **23**, 97–100.

Kehne, H., Willms, L., Ort, O., Bauer, K. & Bieringer, H. (1991). DE Patent A01N47/36, 4000503.

Li, S. J., Zhang, D. C., Cao, Y., Ge, L. P. & Yu, K. B. (2000). *Chin. J. Struct. Chem.* **19**, 99–101.

McCourt, J. A., Pang, S. S., Guddat, L. W. & Duggleby, R. G. (2005). *Biochemistry*, **44**, 2330–2338.

Pu, Q., Sun, D. Q. & Zen, R. S. (1994). *Chin. J. Appl. Chem.* **11**, 101–103.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Takematsu, T. & Akinori, S. (1988). JP Patent A01N47/30, 63211260.

Wang, Z. N. & Xue, S. J. (2001). *Chin. J. Org. Chem.* **21**, 174–177.

Xue, S. J., Ke, S. Y., Duan, L. P., Wang, X. H. & Guo, Y. L. (2005). *J. Indian Chem. Soc.* **1**, 79–82.

Xue, S. J., Zhou, J. S. & Yang H. J. (2000). *Chin. Chem. Lett.* **11**, 19–20.

Zhang, D. C., Zhang, Y. Q., Cao, Y. & Zhao, B. (1996). *Acta Cryst.* C**52**, 1716–1718.