

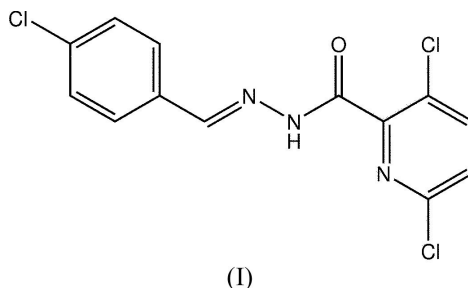
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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.039
 wR factor = 0.102
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(E)-N'-(4-Chlorobenzylidene)-3,6-dichloro-picolinohydrazide**The title compound, $\text{C}_{13}\text{H}_8\text{Cl}_3\text{N}_3\text{O}$, shows the substituted pyridine ring to be twisted by about 10° from the rest of the essentially planar molecule.Received 23 May 2006
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Comment

3,6-Dichloropyridine-2-carboxylic acid is a herbicide which is effective against a variety of weeds (Gaiser, 1989). However, it is also damaging to sensitive plants, including popular agricultural and garden crops such as tomatoes, peppers, potatoes, peas, beans, clover, alfalfa and sunflower, at very low concentrations, down to, and sometimes below, 10 p.p.b. (Lucas & Lobb, 1987; Rynk, 2003). The title compound, (I), has been prepared for evaluation as a substitute for 3,6-dichloropyridine-2-carboxylic acid (Kucukguzel *et al.*, 2003).The molecular structure of (I) (Fig. 1) is essentially planar, albeit with a small twist about the C1–C9 bond. This is substantiated by the values of the C1–N1–N2–C2, N2–C2–C3–C4 and N1–C1–C9–N3 torsion angles of -178.9 (2), -179.5 (2) and -10.7 (3) $^\circ$, respectively. The N1–N2, N1–C1, N2–C2 and C1–O1 bond distances (Table 1) are suggestive of limited delocalization of π -electron density over the central chromophore.The H atom bound to atom N1 is involved in an intramolecular interaction with atom N3 of the pyridine ring, with $\text{H1}\cdots\text{N3} = 2.21$ Å, $\text{N1}\cdots\text{N3} = 2.609$ (3) Å and $\text{N1}-\text{H1}\cdots\text{N3} = 108^\circ$. This atom also forms a weak intermolecular N1–H1 \cdots Cl3ⁱ interaction, with $\text{H1}\cdots\text{Cl3}^i = 2.87$ Å, $\text{N1}\cdots\text{Cl3}^i = 3.515$ (2) Å and $\text{N1}-\text{H1}\cdots\text{Cl3}^i = 134^\circ$ [symmetry code: (i) $x - 1, y, z$].The carbonyl atom O1 is situated in a pocket defined by three aromatic H atoms, being separated from each by 2.6–2.7 Å. The closest interaction between π -systems is 3.70 Å, between the ring centroids of N3/C9–C13 and C3–C8ⁱⁱ [symmetry code: (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$]. This leads to stacks of molecules along the c direction. It appears that the primary connections between stacks are mediated by Cl \cdots Cl interactions, with the closest of these [3.2737 (14) Å] occurring

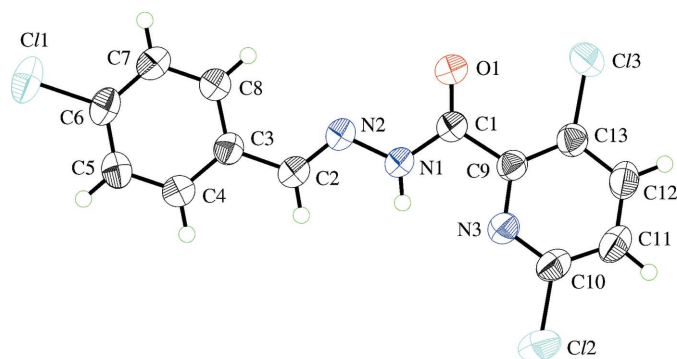


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and with displacement ellipsoids drawn at the 50% probability level.

between atom Cl1 and the centrosymmetrically related atom Cl1ⁱⁱⁱ [symmetry code: (iii) $1 - x, -y, 1 - z$]. Indeed, as seen from Fig. 2, there are distinct chloride-rich regions in the unit cell, where four Cl atoms in the shape of a skewed diamond are connected *via* three Cl \cdots Cl interactions. The aforementioned Cl1 \cdots Cl1^{iv} interactions [symmetry code: (iv) $x, y + 1, z$] are internal to the diamond and the two short edges are defined by Cl1 \cdots Cl2ⁱⁱⁱ contacts of 3.6272 (15) Å. The Cl \cdots Cl separations of the remaining edges are >4 Å.

Experimental

A mixture of 3,6-dichloropyridine-2-carboxylic acid hydrazide (1 g, 4.85 mmol) and 4-chlorobenzaldehyde (0.68 g, 3.32 mmol) in anhydrous ethanol (20 ml) was stirred vigorously at reflux for 0.5 h, following the literature procedure of Kucukguzel *et al.* (2003). The reaction mixture was then filtered and washed with ethanol (30 ml) to give 1.12 g (70.2%) of (I). Yellow crystals (m.p. 491–493 K) were obtained by slow evaporation of an anhydrous ethanol solution of (I) after 5 d at room temperature.

Crystal data

$C_{13}H_8Cl_3N_3O$	$Z = 4$
$M_r = 328.57$	$D_x = 1.553 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.6081 (18) \text{ \AA}$	$\mu = 0.65 \text{ mm}^{-1}$
$b = 14.072 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 15.133 (4) \text{ \AA}$	Block, yellow
$\beta = 92.985 (6)^\circ$	$0.42 \times 0.41 \times 0.37 \text{ mm}$
$V = 1405.3 (7) \text{ \AA}^3$	

Data collection

Siemens SMART CCD area-detector diffractometer	2469 independent reflections
φ and ω scans	2128 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.019$
7694 measured reflections	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.6002P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
2469 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
181 parameters	
H-atom parameters constrained	

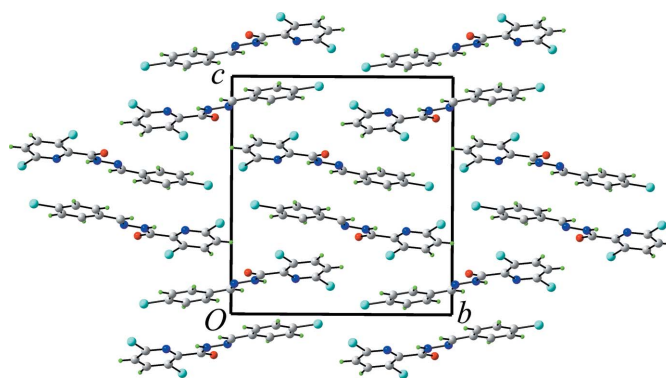


Figure 2
The crystal packing in (I), viewed down the a axis. Colour code: Cl atoms are cyan, O red, N blue, C grey and H green.

Table 1

Selected geometric parameters (Å, °).

Cl1—C6	1.736 (2)	Cl1—N1	1.348 (3)
Cl2—C10	1.736 (2)	C2—N2	1.269 (3)
Cl3—C13	1.731 (2)	N3—C9	1.345 (3)
N1—N2	1.377 (2)	N3—C10	1.314 (3)
C1—O1	1.210 (3)		
N2—N1—C1	120.04 (18)	O1—C1—C9	123.6 (2)
N1—N2—C2	115.51 (19)	N1—C1—C9	112.68 (18)
O1—C1—N1	123.8 (2)		

The H atoms were included in the riding-model approximation, with C—H(aromatic) = 0.93 Å and C—H(methyl) = 0.96 Å, and with $U_{\text{iso}}(\text{H}) = 1.2$ and $1.5U_{\text{eq}}(\text{C})$ for aromatic and methyl-H, respectively.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXL97.

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