

2-(2,4,6-Trichlorophenoxy)ethyl bromide

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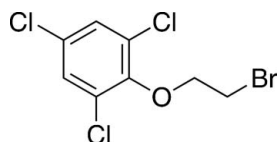
Received 8 October 2009; accepted 20 October 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.045; wR factor = 0.123; data-to-parameter ratio = 16.3.

In the title compound, $\text{C}_8\text{H}_6\text{BrCl}_3\text{O}$, there is a weak intramolecular $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bond involving the O bound methylene group. Intermolecular $\text{Cl}\cdots\text{Cl}$ contacts [$3.482(2)$ Å] are present in the crystal structure.

Related literature

The title compound is used as an intermediate in the production of Prochloraz, a broad-spectrum imidazole fungicide widely used in gardening and agriculture. For the fungicidal properties of Prochloraz, see: Copping *et al.* (1984). For the preparation, see: Howard & Alfred (1982). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_8\text{H}_6\text{BrCl}_3\text{O}$
 $M_r = 304.39$
Triclinic, $P\bar{1}$
 $a = 4.0550(8)$ Å

$b = 8.6270(17)$ Å
 $c = 15.183(3)$ Å
 $\alpha = 90.73(3)^\circ$
 $\beta = 94.81(3)^\circ$

$\gamma = 90.42(3)^\circ$
 $V = 529.21(18)$ Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 4.60$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.10 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.460$, $T_{\max} = 0.656$
2215 measured reflections

1919 independent reflections
1280 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.123$
 $S = 1.01$
1919 reflections

118 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.37$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2A}\cdots\text{Cl3}$	0.97	2.81	3.276 (6)	110

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

This research work was financially supported by the Department of Science and Technology of Jiangsu Province (BE200830457) and the '863' project (2007 A A02Z211) of the Ministry of Science and Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2217).

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supplementary materials

Acta Cryst. (2009). E65, o2850 [doi:10.1107/S1600536809043256]

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Comment

Prochloraz, *N*-propyl-*N*-[2-(2,4,6-trichlorophenoxy)-ethyl] -1*H*-imidazole-1-carboxamide, is a broad-spectrum imidazole fungicide (Copping *et al.*, 1984). As part of our studies in the synthesis of Prochloraz, the title compound (I), which is used as the key intermediate, has been synthesized. We report herein the crystal structure of the title compound.

In the molecule of the title compound (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). In the crystal structure, intramolecular C—H···Cl interactions (Table 1) may be effective in the stabilization of the structure.

Experimental

The title compound was prepared by following a reported procedure (Howard & Alfred, 1982). 2,4,6-Trichlorophenol (15.8 g) and sodium hydroxide (4.8 g) were dissolved in 28 ml water and added dropwise to an excess of ethylene dibromide (75.6 g). The reaction mixture was heated under reflux for ten hours. The residue was extracted with 3 x 20 ml dichloromethane, and then methylene chloride phase was washed with water, dried and evaporated to dryness under reduced pressure. Fractionation under reduced pressure yielded the title compound as a colorless oil which was then cooled to give 18.1 g white solid (75.2%). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an ethanol solution of (I).

Refinement

H atoms were positioned geometrically with C—H = 0.93 and 0.97 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$.

Figures

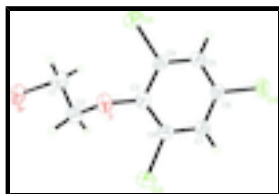


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability levels.

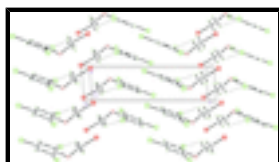


Fig. 2. A packing diagram of the title compound. Intramolecular hydrogen bonds are shown as dashed lines.

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Crystal data

$C_8H_6BrCl_3O$	$Z = 2$
$M_r = 304.39$	$F_{000} = 296$
Triclinic, $P\bar{1}$	$D_x = 1.910 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 4.0550 (8) \text{ \AA}$	Cell parameters from 25 reflections
$b = 8.6270 (17) \text{ \AA}$	$\theta = 10\text{--}14^\circ$
$c = 15.183 (3) \text{ \AA}$	$\mu = 4.60 \text{ mm}^{-1}$
$\alpha = 90.73 (3)^\circ$	$T = 293 \text{ K}$
$\beta = 94.81 (3)^\circ$	Block, colorless
$\gamma = 90.42 (3)^\circ$	$0.20 \times 0.10 \times 0.10 \text{ mm}$
$V = 529.21 (18) \text{ \AA}^3$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.041$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 25.3^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 1.4^\circ$
$T = 293 \text{ K}$	$h = 0 \rightarrow 4$
$\omega/2\theta$ scans	$k = -10 \rightarrow 10$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$l = -18 \rightarrow 18$
$T_{\text{min}} = 0.460$, $T_{\text{max}} = 0.656$	3 standard reflections
2215 measured reflections	every 200 reflections
1919 independent reflections	intensity decay: 1%
1280 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.123$	$w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
1919 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
118 parameters	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.06298 (16)	0.24181 (8)	-0.05453 (4)	0.0696 (3)
O	0.6382 (9)	0.3089 (4)	0.1806 (2)	0.0537 (9)
Cl1	0.6363 (4)	-0.01264 (17)	0.24134 (11)	0.0689 (5)
Cl2	0.1372 (4)	0.22953 (19)	0.52835 (10)	0.0707 (5)
Cl3	0.4167 (5)	0.59982 (17)	0.26392 (11)	0.0777 (5)
C1	0.3028 (15)	0.1966 (7)	0.0606 (4)	0.0651 (16)
H1A	0.1585	0.1417	0.0977	0.078*
H1B	0.4922	0.1318	0.0521	0.078*
C2	0.4125 (15)	0.3430 (7)	0.1030 (4)	0.0609 (15)
H2A	0.2235	0.4002	0.1208	0.073*
H2B	0.5249	0.4058	0.0620	0.073*
C3	0.5043 (12)	0.2915 (6)	0.2586 (3)	0.0436 (12)
C4	0.4945 (12)	0.1458 (6)	0.2977 (4)	0.0467 (13)
C5	0.3811 (13)	0.1253 (6)	0.3795 (3)	0.0486 (13)
H5A	0.3760	0.0273	0.4042	0.058*
C6	0.2752 (13)	0.2530 (6)	0.4241 (3)	0.0476 (13)
C7	0.2808 (13)	0.3971 (6)	0.3887 (4)	0.0506 (14)
H7A	0.2071	0.4822	0.4195	0.061*
C8	0.3966 (13)	0.4152 (6)	0.3068 (4)	0.0482 (13)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0586 (4)	0.0971 (5)	0.0522 (4)	0.0021 (3)	0.0018 (3)	-0.0099 (3)
O	0.045 (2)	0.070 (2)	0.046 (2)	0.0014 (18)	0.0040 (19)	0.0043 (18)
Cl1	0.0775 (11)	0.0580 (9)	0.0722 (10)	0.0176 (8)	0.0128 (9)	-0.0101 (7)
Cl2	0.0801 (11)	0.0855 (11)	0.0482 (9)	0.0115 (9)	0.0131 (8)	0.0051 (8)
Cl3	0.1140 (14)	0.0486 (8)	0.0695 (11)	-0.0029 (9)	0.0020 (10)	0.0059 (7)
C1	0.053 (4)	0.069 (4)	0.075 (4)	-0.002 (3)	0.018 (3)	0.002 (3)
C2	0.062 (4)	0.058 (3)	0.064 (4)	-0.001 (3)	0.016 (3)	0.004 (3)
C3	0.033 (3)	0.052 (3)	0.045 (3)	0.001 (2)	-0.001 (2)	-0.003 (2)
C4	0.044 (3)	0.045 (3)	0.051 (3)	0.008 (2)	-0.001 (3)	-0.007 (2)

supplementary materials

C5	0.049 (3)	0.046 (3)	0.051 (3)	0.004 (2)	0.003 (3)	0.003 (3)
C6	0.041 (3)	0.059 (3)	0.042 (3)	0.005 (3)	-0.005 (2)	-0.001 (3)
C7	0.052 (3)	0.050 (3)	0.050 (3)	0.009 (3)	-0.002 (3)	-0.004 (3)
C8	0.048 (3)	0.041 (3)	0.054 (3)	0.001 (2)	-0.003 (3)	0.001 (2)

Geometric parameters (\AA , $^\circ$)

Br—C1	1.973 (6)	C2—H2B	0.9700
O—C3	1.353 (6)	C3—C8	1.380 (7)
O—C2	1.464 (7)	C3—C4	1.398 (7)
C11—C4	1.731 (5)	C4—C5	1.373 (7)
C12—C6	1.737 (5)	C5—C6	1.376 (7)
C13—C8	1.733 (5)	C5—H5A	0.9300
C1—C2	1.459 (8)	C6—C7	1.361 (7)
C1—H1A	0.9700	C7—C8	1.375 (8)
C1—H1B	0.9700	C7—H7A	0.9300
C2—H2A	0.9700		
C3—O—C2	117.4 (4)	C5—C4—C3	122.1 (5)
C2—C1—Br	108.5 (4)	C5—C4—C11	119.2 (4)
C2—C1—H1A	110.0	C3—C4—C11	118.6 (4)
Br—C1—H1A	110.0	C4—C5—C6	118.5 (5)
C2—C1—H1B	110.0	C4—C5—H5A	120.8
Br—C1—H1B	110.0	C6—C5—H5A	120.8
H1A—C1—H1B	108.4	C7—C6—C5	121.4 (5)
C1—C2—O	108.5 (5)	C7—C6—C12	119.5 (4)
C1—C2—H2A	110.0	C5—C6—C12	119.1 (4)
O—C2—H2A	110.0	C6—C7—C8	119.2 (5)
C1—C2—H2B	110.0	C6—C7—H7A	120.4
O—C2—H2B	110.0	C8—C7—H7A	120.4
H2A—C2—H2B	108.4	C7—C8—C3	122.1 (5)
O—C3—C8	122.7 (5)	C7—C8—C13	118.9 (4)
O—C3—C4	120.4 (4)	C3—C8—C13	118.9 (4)
C8—C3—C4	116.7 (5)		
Br—C1—C2—O	-170.3 (3)	C4—C5—C6—C7	0.1 (8)
C3—O—C2—C1	-90.6 (6)	C4—C5—C6—C12	-179.0 (4)
C2—O—C3—C8	-75.1 (6)	C5—C6—C7—C8	-0.4 (8)
C2—O—C3—C4	110.3 (5)	C12—C6—C7—C8	178.7 (4)
O—C3—C4—C5	175.5 (5)	C6—C7—C8—C3	0.8 (8)
C8—C3—C4—C5	0.6 (7)	C6—C7—C8—C13	-177.7 (4)
O—C3—C4—C11	-3.4 (6)	O—C3—C8—C7	-175.7 (5)
C8—C3—C4—C11	-178.4 (4)	C4—C3—C8—C7	-0.9 (8)
C3—C4—C5—C6	-0.2 (8)	O—C3—C8—C13	2.8 (7)
C11—C4—C5—C6	178.8 (4)	C4—C3—C8—C13	177.7 (4)

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

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
C2—H2A \cdots C13	0.97	2.81	3.276 (6)	110

Fig. 1

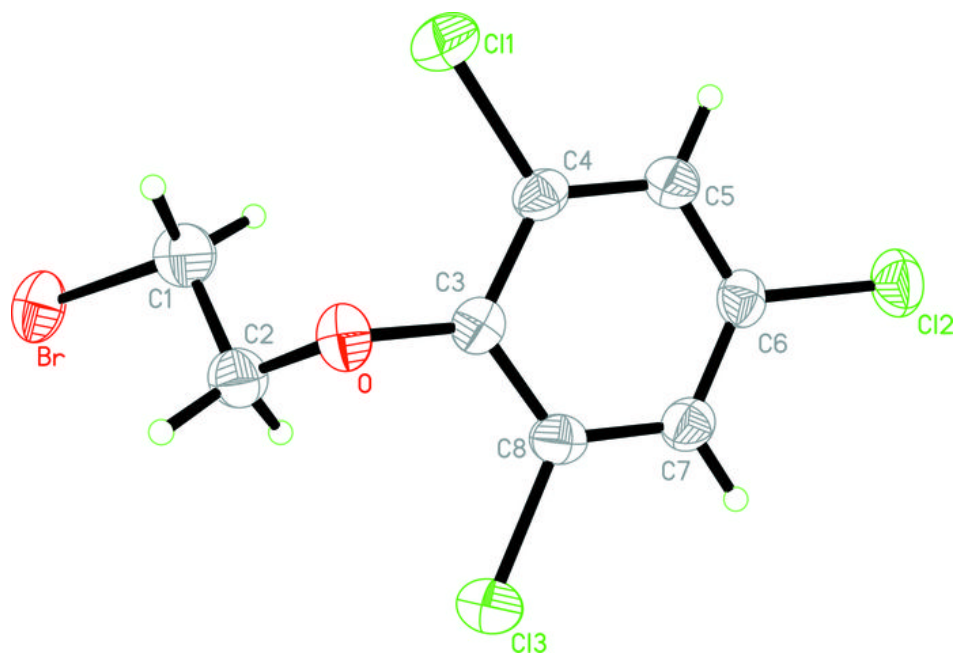


Fig. 2

