Crystal structure of metobromuron

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The title compound [systematic name: 3-(4-bromophenyl)-1-methoxy-1-methylurea], $C_9H_{11}BrN_2O_2$, is a phenylurea herbicide. The dihedral angle between the plane of the urea group and that of the bromophenyl ring is 39.13 (10)°. In the crystal, N—H⋯O and C—H⋯O hydrogen bonds and weak C—H⋯π interactions link adjacent molecules, forming chains along the a-axis direction. In addition, short intermolecular Br⋯Br contacts [3.648 (4) Å] are present, resulting in a two-dimensional network extending parallel to (101).

1. Related literature

For information on the herbicidal properties of the title compound, see: Leila et al. (2011). For related crystal structures, see: Black et al. (2010); Kostyanovsky et al. (2010).
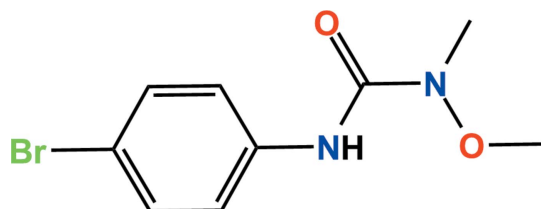
2. Experimental

2.1. Crystal data

$C_9H_{11}BrN_2O_2$
$M_r = 259.11$

Orthorhombic, Pbca
$a = 9.8184$ (2) Å
$b = 11.3286$ (3) Å
$c = 18.9569$ (5) Å
$V = 2108.55$ (9) Å³
$Z = 8$

Mo $K\alpha$ radiation
$\mu = 3.88$ mm⁻¹
$T = 173$ K
$0.30 \times 0.16 \times 0.02$ mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2013)
$T_{min} = 0.389$, $T_{max} = 0.927$

17922 measured reflections
2424 independent reflections
1857 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.066$
$S = 1.03$
2424 reflections

129 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.41$ e Å⁻³
$\Delta\rho_{min} = -0.42$ e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N⋯O1ⁱ	0.88	2.39	3.130 (2)	142
C2—H2⋯O1ⁱ	0.95	2.42	3.217 (3)	142
C9—H9A⋯Cg1ⁱ	0.98	2.99	3.477 (3)	112

Symmetry code: (i) $x - \frac{1}{2}, y, -z + \frac{3}{2}$.

Data collection: APEX2 (Bruker, 2013); cell refinement: SAINT (Bruker, 2013); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2015); molecular graphics: DIAMOND (Brandenburg, 2010); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

Acknowledgements

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S1. Comment

Metobromuron: 3-(4-bromophenyl)-1-methoxy-1-methylurea, is a phenylurea herbicide and has been used for the control of broadleaf weeds in cereal and vegetable crops, acting through the inhibition of photosynthesis (Leila *et al.*, 2011). However, until now its crystal structure has not been reported. In the title compound (Fig. 1), the dihedral angle between the plane of the urea group and the bromophenyl ring is 39.13 (10) °. All bond lengths and bond angles are normal and comparable to those observed in similar crystal structures (Black *et al.*, 2010; Kostyanovsky *et al.*, 2010).

In the crystal structure (Fig. 2), N–H···O and C–H···O hydrogen bonds and weak C–H···π interactions link adjacent molecules (Table 1), forming one-dimensional chains along the *a*-axis direction. In addition, weak intermolecular short Br···Br contacts [3.648 (4) Å] are present, resulting in a two-dimensional network extending parallel to (101).

S2. Experimental

The title compound was purchased from the Dr. Ehrenstorfer GmbH Company. Slow evaporation of a solution in ethyl acetate gave single crystals suitable for X-ray analysis.

S3. Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(N—H) = 0.88 Å, U_{iso} = 1.2U_{eq}(C) for urea N—H, d(C—H) = 0.98 Å, U_{iso} = 1.5U_{eq}(C) for methyl group, d(C—H) = 0.95 Å, U_{iso} = 1.2U_{eq}(C) for aromatic C—H.
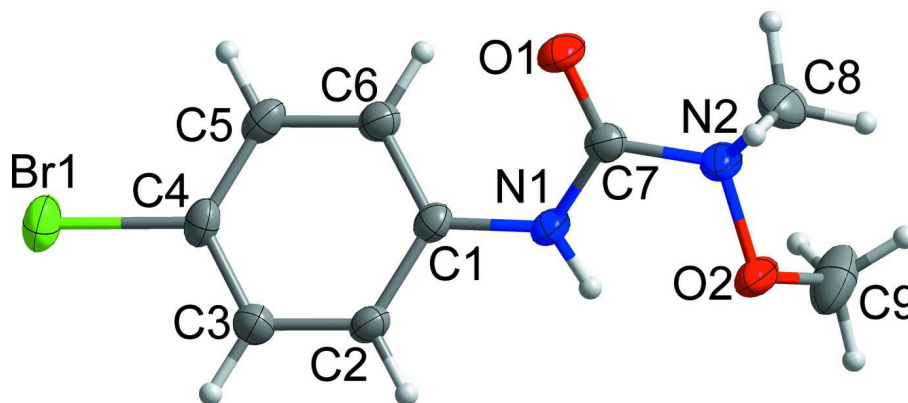

Figure 1

The asymmetric unit of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.
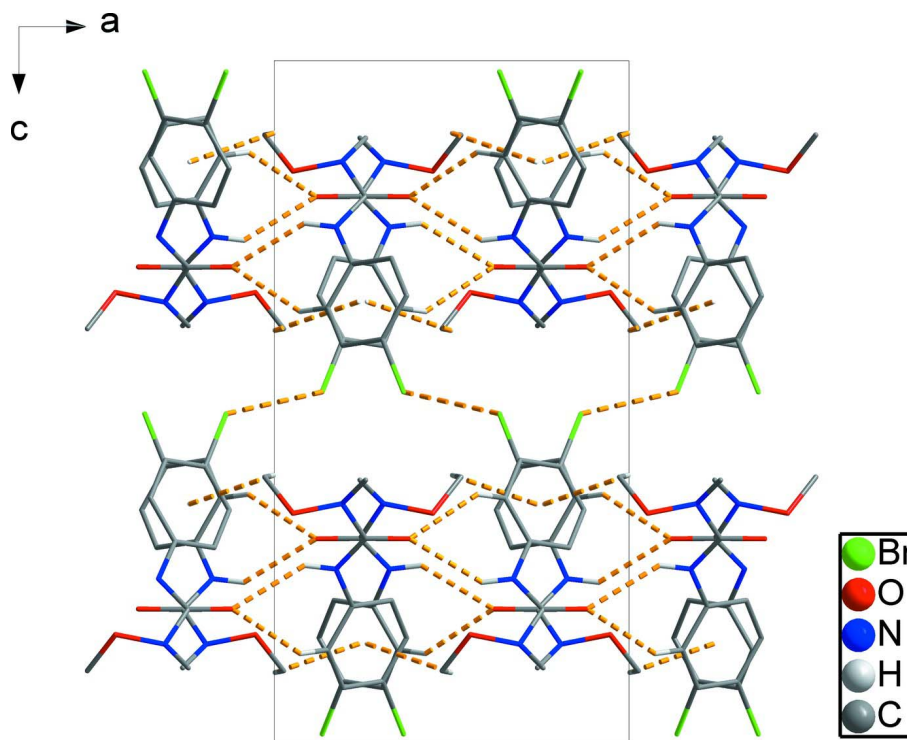
Figure 2

Crystal packing viewed along the *b* axis. The intermolecular interactions are shown as dashed lines.

3-(4-Bromophenyl)-1-methoxy-1-methylurea

Crystal data

$C_9H_{11}BrN_2O_2$	$D_x = 1.632$ Mg m^{-3}
$M_r = 259.11$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 3544 reflections
$a = 9.8184$ (2) Å	$\theta = 3.0$–24.1°
$b = 11.3286$ (3) Å	$\mu = 3.88$ mm^{-1}
$c = 18.9569$ (5) Å	$T = 173$ K
$V = 2108.55$ (9) Å^3	Plate, colourless
$Z = 8$	$0.30 \times 0.16 \times 0.02$ mm
$F(000) = 1040$	

Data collection

Bruker APEXII CCD diffractometer	2424 independent reflections
φ and ω scans	1857 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)	$R_{int} = 0.048$
	$\theta_{max} = 27.5°$, $\theta_{min} = 2.2°$
$T_{min} = 0.389$, $T_{max} = 0.927$	$h = -12 \rightarrow 12$
17922 measured reflections	$k = -14 \rightarrow 14$
	$l = -23 \rightarrow 24$

Refinement

Refinement on F^2	$S = 1.03$
Least-squares matrix: full	2424 reflections
$R[F^2 > 2\sigma(F^2)] = 0.029$	129 parameters
$wR(F^2) = 0.066$	0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 1.105P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.86464 (3)	0.10694 (2)	0.51608 (2)	0.03673 (10)
O1	0.88255 (14)	0.47320 (14)	0.80131 (9)	0.0337 (4)
O2	0.55297 (15)	0.56454 (15)	0.83862 (9)	0.0338 (4)
N1	0.67399 (18)	0.41832 (16)	0.75709 (10)	0.0259 (4)
H1N	0.5855	0.4269	0.7624	0.031*
N2	0.69171 (18)	0.54270 (17)	0.85274 (10)	0.0297 (5)
C1	0.7206 (2)	0.34339 (18)	0.70276 (12)	0.0224 (5)
C2	0.6508 (2)	0.34425 (19)	0.63907 (12)	0.0249 (5)
H2	0.5732	0.3934	0.6335	0.030*
C3	0.6936 (2)	0.2741 (2)	0.58381 (12)	0.0276 (5)
H3	0.6467	0.2756	0.5400	0.033*
C4	0.8053 (2)	0.20197 (19)	0.59297 (12)	0.0265 (5)
C5	0.8734 (2)	0.19632 (19)	0.65655 (12)	0.0278 (5)
H5	0.9485	0.1444	0.6625	0.033*
C6	0.8306 (2)	0.26736 (19)	0.71147 (12)	0.0264 (5)
H6	0.8766	0.2643	0.7555	0.032*
C7	0.7577 (2)	0.47817 (19)	0.80181 (12)	0.0248 (5)
C8	0.7580 (3)	0.6412 (2)	0.88719 (14)	0.0378 (6)
H8A	0.8452	0.6152	0.9069	0.057*
H8B	0.6996	0.6709	0.9252	0.057*
H8C	0.7740	0.7042	0.8528	0.057*
C9	0.4734 (3)	0.5087 (3)	0.89159 (16)	0.0525 (8)
H9A	0.4974	0.4249	0.8941	0.079*
H9B	0.3766	0.5168	0.8800	0.079*
H9C	0.4914	0.5461	0.9373	0.079*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.04164 (16)	0.03414 (14)	0.03440 (17)	0.00799 (11)	0.01142 (11)	−0.00470 (11)
O1	0.0172 (9)	0.0434 (10)	0.0404 (10)	0.0032 (7)	−0.0014 (7)	−0.0051 (8)
O2	0.0191 (8)	0.0430 (10)	0.0395 (10)	0.0057 (7)	−0.0011 (7)	−0.0108 (8)
N1	0.0157 (9)	0.0335 (11)	0.0285 (11)	0.0028 (7)	0.0012 (8)	−0.0047 (9)
N2	0.0195 (10)	0.0382 (12)	0.0314 (12)	0.0014 (8)	−0.0023 (8)	−0.0082 (9)

C1	0.0194 (11)	0.0238 (11)	0.0241 (12)	0.0008 (8)	0.0040 (9)	0.0012 (9)
C2	0.0203 (12)	0.0278 (11)	0.0267 (13)	0.0060 (9)	0.0009 (9)	0.0021 (10)
C3	0.0275 (12)	0.0311 (12)	0.0241 (13)	0.0037 (9)	−0.0005 (10)	0.0014 (10)
C4	0.0282 (12)	0.0256 (11)	0.0255 (13)	0.0023 (9)	0.0092 (10)	0.0001 (10)
C5	0.0229 (12)	0.0254 (11)	0.0350 (14)	0.0057 (9)	0.0063 (10)	0.0046 (10)
C6	0.0235 (12)	0.0301 (12)	0.0254 (12)	0.0034 (9)	0.0009 (9)	0.0033 (10)
C7	0.0223 (12)	0.0273 (11)	0.0249 (12)	0.0011 (9)	0.0003 (9)	0.0032 (9)
C8	0.0338 (14)	0.0426 (15)	0.0371 (15)	−0.0010 (11)	−0.0087 (12)	−0.0110 (12)
C9	0.0383 (16)	0.0555 (18)	0.064 (2)	−0.0075 (13)	0.0224 (15)	−0.0177 (16)

Geometric parameters (Å, º)

Br1—C4	1.904 (2)	C3—C4	1.378 (3)
O1—C7	1.228 (3)	C3—H3	0.9500
O2—N2	1.410 (2)	C4—C5	1.380 (3)
O2—C9	1.421 (3)	C5—C6	1.381 (3)
N1—C7	1.361 (3)	C5—H5	0.9500
N1—C1	1.411 (3)	C6—H6	0.9500
N1—H1N	0.8800	C8—H8A	0.9800
N2—C7	1.373 (3)	C8—H8B	0.9800
N2—C8	1.448 (3)	C8—H8C	0.9800
C1—C2	1.388 (3)	C9—H9A	0.9800
C1—C6	1.391 (3)	C9—H9B	0.9800
C2—C3	1.380 (3)	C9—H9C	0.9800
C2—H2	0.9500		

N2—O2—C9	108.60 (19)	C4—C5—H5	120.5
C7—N1—C1	123.95 (18)	C6—C5—H5	120.5
C7—N1—H1N	118.0	C5—C6—C1	120.5 (2)
C1—N1—H1N	118.0	C5—C6—H6	119.8
C7—N2—O2	114.55 (17)	C1—C6—H6	119.8
C7—N2—C8	121.04 (19)	O1—C7—N1	125.1 (2)
O2—N2—C8	112.62 (18)	O1—C7—N2	120.1 (2)
C2—C1—C6	119.4 (2)	N1—C7—N2	114.73 (19)
C2—C1—N1	118.07 (19)	N2—C8—H8A	109.5
C6—C1—N1	122.5 (2)	N2—C8—H8B	109.5
C3—C2—C1	120.4 (2)	H8A—C8—H8B	109.5
C3—C2—H2	119.8	N2—C8—H8C	109.5
C1—C2—H2	119.8	H8A—C8—H8C	109.5
C4—C3—C2	119.2 (2)	H8B—C8—H8C	109.5
C4—C3—H3	120.4	O2—C9—H9A	109.5
C2—C3—H3	120.4	O2—C9—H9B	109.5
C3—C4—C5	121.5 (2)	H9A—C9—H9B	109.5
C3—C4—Br1	118.85 (18)	O2—C9—H9C	109.5
C5—C4—Br1	119.62 (16)	H9A—C9—H9C	109.5
C4—C5—C6	119.0 (2)	H9B—C9—H9C	109.5

C9—O2—N2—C7	116.7 (2)	Br1—C4—C5—C6	178.85 (16)

C9—O2—N2—C8	−99.8 (2)	C4—C5—C6—C1	0.0 (3)
C7—N1—C1—C2	−141.5 (2)	C2—C1—C6—C5	2.3 (3)
C7—N1—C1—C6	40.2 (3)	N1—C1—C6—C5	−179.4 (2)
C6—C1—C2—C3	−2.8 (3)	C1—N1—C7—O1	−1.2 (4)
N1—C1—C2—C3	178.9 (2)	C1—N1—C7—N2	−177.6 (2)
C1—C2—C3—C4	0.9 (3)	O2—N2—C7—O1	165.9 (2)
C2—C3—C4—C5	1.4 (3)	C8—N2—C7—O1	25.7 (3)
C2—C3—C4—Br1	−179.30 (17)	O2—N2—C7—N1	−17.6 (3)
C3—C4—C5—C6	−1.9 (3)	C8—N2—C7—N1	−157.8 (2)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1ⁱ	0.88	2.39	3.130 (2)	142
C2—H2···O1ⁱ	0.95	2.42	3.217 (3)	142
C9—H9*A*···*Cg*1ⁱ	0.98	2.99	3.477 (3)	112

Symmetry code: (i) $x-1/2$, y, $-z+3/2$.