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1-(4-Bromo-3-chlorophenyl)-3-methoxy-3-methylurea (chlorbromuron)

Harrison M. Black and Russell G. Baughman*

Department of Chemistry, Truman State University, Kirksville, MO 63501-4221, USA
Correspondence e-mail: baughman@truman.edu

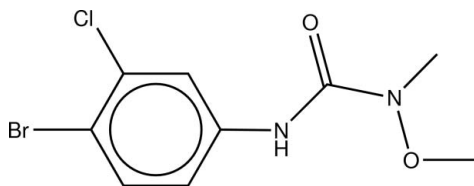
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å;
 R factor = 0.065; wR factor = 0.173; data-to-parameter ratio = 14.8.

In the title urea-based herbicide, $\text{C}_9\text{H}_{10}\text{BrClN}_2\text{O}_2$, there exist multiple inter- and intramolecular interactions. Most notably, the intramolecular hydrogen bond between the urea carbonyl O atom and an aromatic H atom affects the planarity and torsion angles of the molecule by restricting rotations about the Ar—secondary amine N and the secondary amine N and the carbonyl C. The two N atoms in the urea fragment are in different environments. One is planar; the other, pseudo- C_{3v} . It is likely that the different nitrogen-atom geometries and the restricted rotations within the molecule impact the bioactivity of chlorbromuron.

Related literature

The structure of the title compound, chlorbromuron, was determined as part of a larger project on the crystal and molecular structures of a series of herbicides, see: Baughman & Yu (1988 and references cited therein). Chlorbromuron is a urea-based herbicide that acts to inhibit photosynthesis and the oxidation of water to oxygen during the Hill reaction, see: Metcalf (1971). Typically one or more hydrogen bonds form between the $-\text{NH}-$ or $\text{C}=\text{O}$ groups in the urea-based herbicides and an active site in the protein, see: Good (1961).



Experimental

Crystal data

 $\text{C}_9\text{H}_{10}\text{BrClN}_2\text{O}_2$ $M_r = 293.55$ Orthorhombic, $Pbca$ $a = 11.3872$ (7) Å $b = 9.5037$ (5) Å $c = 21.512$ (2) Å $V = 2328.0$ (3) Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 3.74$ mm⁻¹ $T = 295$ K $0.44 \times 0.44 \times 0.42$ mm

Data collection

Bruker P4 diffractometer

Absorption correction: integration

(XSELL; Bruker, 1999)

 $T_{\min} = 0.224$, $T_{\max} = 0.331$

2643 measured reflections

2017 independent reflections

1230 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.107$

3 standard reflections every 100 reflections

intensity decay: 1.3%

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.065$ $wR(F^2) = 0.173$ $S = 0.99$

2017 reflections

136 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 1.13$ e Å⁻³ $\Delta\rho_{\min} = -0.63$ e Å⁻³

Table 1

Selected torsion angles (°).

| | | | |
|-------------|------------|-------------|----------|
| C9—O2—N2—C7 | −124.6 (6) | C7—N1—C1—C2 | 23.3 (9) |
| C9—O2—N2—C8 | 97.8 (7) | O2—N2—C7—N1 | 20.2 (7) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------|-------|-------------|-------------|---------------|
| N1—H1 \cdots O1 ¹ | 0.86 | 2.11 | 2.902 (7) | 153 |
| N1—H1 \cdots O2 | 0.86 | 2.18 | 2.573 (6) | 108 |
| C2—H2 \cdots O1 | 0.93 | 2.35 | 2.873 (7) | 115 |

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

Data collection: XSCANS (Bruker, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS86 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL/PC (Sheldrick, 2008); software used to prepare material for publication: SHELXTL/PC and SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2148).

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supplementary materials

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1-(4-Bromo-3-chlorophenyl)-3-methoxy-3-methylurea (chlorbromuron)

H. M. Black and R. G. Baughman

Comment

The crystal structure of 3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea, chlorbromuron (I), was determined as part of a larger project (Baughman and Yu, 1988 and references cited therein) that has focused on the crystal and molecular structures of a series of herbicides. Chlorbromuron is a urea-based herbicide that acts to inhibit photosynthesis and the oxidation of water to oxygen during the Hill reaction (Metcalf, 1971). Typically one or more hydrogen bonds form between the -NH- or C=O groups in the urea-based herbicides and an active site in the protein (Good, 1961).

Molecules in the unit cell utilize intermolecular hydrogen bonds, while the molecule contains intramolecular hydrogen bonds. The $\text{O1}\cdots\text{H1}$ intermolecular hydrogen bond and the $\text{O2}\cdots\text{H1}$ and $\text{O1}\cdots\text{H2}$ intramolecular hydrogen bonds affect the torsion angles (Table 1). The $\text{O1}\cdots\text{H2}$ hydrogen bond is interesting because it likely causes H2/C2/C1/N1/C7/O1 to be nearly planar (r.m.s. deviation = 0.167 Å). Similarly, the O2-N2-C7-N1 torsion angle of $20.2(7)^\circ$ and near planarity of H1A/N1/C7/N2/O2 (r.m.s. = 0.100 Å) indicate the effect of the $\text{O2}\cdots\text{H1}$ hydrogen bond.

Since the $\text{O1}\cdots\text{H2}$ and $\text{O2}\cdots\text{H1}$ intramolecular hydrogen bonds limit rotation, the structure of (I) presented here may also be close to that *in vitro* and/or *in vivo*. The limiting of the rotational degrees of freedom about the C1-N1 , N1-C7 , and C7-N2 bonds may influence the bioactivity of (I). A very weak intermolecular interaction between Cl1 and H9A likely exists, but, at a distance of 3.15 Å, is a little too long to be considered a true hydrogen bond, but may have some impact on packing.

Structurally significant angles around N2 indicate a pseudo- C_{3v} shape (Fig. 1, Table 1). However, the geometry around N1 is planar. Although the C4-C3-Cl1 angle [$121.1(5)^\circ$] is $\sim 2\sigma$ greater than the ideal angle of 120° , the C3-C4-Br1 angle [$122.3(5)^\circ$] is $\sim 5\sigma$ greater than ideal angle, which indicates some steric and charge repulsion in this portion of the molecule.

Experimental

Crystals were grown by slow evaporation of a solution in EtOH.

Refinement

Approximate positions of all H's were first obtained from a difference map, then placed into "ideal" positions. Bond lengths were constrained at 0.93 Å (AFIX 43) for aromatic C-H's, at 0.96 Å (AFIX 137) for methyl C-H's, and 0.86 Å (AFIX 43) for the N-H.

$U_{\text{iso}}(\text{H})$ were fixed at $1.5U_{\text{eq}}(\text{parent})$ for OH and methyl H's, and $1.2U_{\text{eq}}(\text{parent})$ for all other H's.

In the final stages of refinement for (I), 14 very small or negative F_o 's were deemed to be in high disagreement and were eliminated from final refinement.

Percent decay of the three standards was calculated as the average of their $\sigma(I)$'s.

Figures

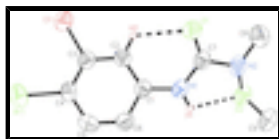


Fig. 1. The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability levels; H atoms are drawn as small spheres of arbitrary radius.

1-(4-Bromo-3-chlorophenyl)-3-methoxy-3-methylurea

Crystal data

$C_9H_{10}BrClN_2O_2$

$M_r = 293.55$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 11.3872$ (7) Å

$b = 9.5037$ (5) Å

$c = 21.512$ (2) Å

$V = 2328.0$ (3) Å³

$Z = 8$

$F(000) = 1168$

$D_x = 1.675$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 100 reflections

$\theta = 10.0$ – 15.8°

$\mu = 3.74$ mm⁻¹

$T = 295$ K

Rectangular prism, colorless

$0.44 \times 0.44 \times 0.42$ mm

Data collection

Bruker P4
diffractometer

Radiation source: normal-focus sealed tube
graphite

Ω scans

Absorption correction: integration
(XSHHELL; Bruker, 1999)

$T_{\min} = 0.224$, $T_{\max} = 0.331$

2643 measured reflections

2017 independent reflections

1230 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.107$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -1 \rightarrow 13$

$k = -11 \rightarrow 1$

$l = -25 \rightarrow 1$

3 standard reflections every 100 reflections

intensity decay: 1.3%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.173$

$S = 0.99$

2017 reflections

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1011P)^2 + 0.010P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

136 parameters

$$\Delta\rho_{\max} = 1.13 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.63 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|-------------|----------------------------------|
| Br1 | 0.99321 (6) | 0.13975 (8) | 0.40066 (3) | 0.0648 (4) |
| Cl1 | 0.75978 (19) | -0.0374 (2) | 0.44369 (7) | 0.0690 (6) |
| O1 | 0.6655 (4) | 0.0148 (4) | 0.6675 (2) | 0.0571 (12) |
| O2 | 0.6463 (4) | 0.3363 (4) | 0.7430 (2) | 0.0560 (12) |
| N1 | 0.7597 (4) | 0.2249 (5) | 0.6520 (2) | 0.0424 (12) |
| H1 | 0.7741 | 0.3050 | 0.6690 | 0.051* |
| N2 | 0.6419 (5) | 0.1877 (5) | 0.7384 (2) | 0.0501 (14) |
| C1 | 0.8124 (5) | 0.1972 (6) | 0.5945 (3) | 0.0389 (14) |
| C2 | 0.7677 (6) | 0.1002 (6) | 0.5513 (3) | 0.0449 (15) |
| H2 | 0.7011 | 0.0479 | 0.5609 | 0.054* |
| C3 | 0.8216 (5) | 0.0839 (6) | 0.4948 (3) | 0.0457 (15) |
| C4 | 0.9200 (5) | 0.1589 (6) | 0.4788 (3) | 0.0443 (15) |
| C5 | 0.9659 (5) | 0.2525 (7) | 0.5221 (3) | 0.0506 (17) |
| H5 | 1.0328 | 0.3040 | 0.5121 | 0.061* |
| C6 | 0.9133 (6) | 0.2707 (6) | 0.5784 (3) | 0.0466 (15) |
| H6 | 0.9457 | 0.3331 | 0.6070 | 0.056* |
| C7 | 0.6870 (6) | 0.1363 (7) | 0.6830 (3) | 0.0429 (15) |
| C8 | 0.5314 (7) | 0.1313 (8) | 0.7610 (4) | 0.074 (2) |
| H8A | 0.5320 | 0.0306 | 0.7571 | 0.111* |
| H8B | 0.5204 | 0.1565 | 0.8038 | 0.111* |
| H8C | 0.4684 | 0.1693 | 0.7366 | 0.111* |
| C9 | 0.7083 (8) | 0.3723 (8) | 0.7985 (3) | 0.079 (2) |
| H9A | 0.7121 | 0.4729 | 0.8023 | 0.118* |
| H9B | 0.6691 | 0.3336 | 0.8341 | 0.118* |
| H9C | 0.7864 | 0.3348 | 0.7960 | 0.118* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|------------|------------|------------|
| Br1 | 0.0657 (5) | 0.0802 (6) | 0.0485 (5) | 0.0019 (4) | 0.0147 (4) | 0.0053 (4) |

supplementary materials

| | | | | | | |
|-----|-------------|-------------|------------|--------------|-------------|-------------|
| Cl1 | 0.0940 (14) | 0.0718 (12) | 0.0412 (9) | -0.0225 (10) | 0.0052 (10) | -0.0125 (9) |
| O1 | 0.084 (3) | 0.038 (3) | 0.049 (3) | -0.006 (2) | 0.007 (3) | -0.005 (2) |
| O2 | 0.071 (3) | 0.047 (2) | 0.051 (3) | 0.007 (2) | 0.003 (2) | -0.013 (2) |
| N1 | 0.049 (3) | 0.037 (3) | 0.041 (3) | 0.003 (2) | -0.001 (3) | -0.008 (2) |
| N2 | 0.065 (4) | 0.042 (3) | 0.043 (3) | 0.006 (3) | 0.009 (3) | -0.007 (2) |
| C1 | 0.043 (3) | 0.033 (3) | 0.041 (3) | 0.008 (3) | -0.001 (3) | 0.000 (3) |
| C2 | 0.051 (4) | 0.042 (3) | 0.042 (3) | -0.002 (3) | 0.005 (3) | 0.005 (3) |
| C3 | 0.053 (4) | 0.043 (3) | 0.041 (4) | 0.000 (3) | -0.002 (3) | 0.001 (3) |
| C4 | 0.041 (4) | 0.051 (4) | 0.040 (3) | 0.009 (3) | 0.005 (3) | 0.002 (3) |
| C5 | 0.039 (3) | 0.047 (4) | 0.065 (5) | -0.006 (3) | 0.000 (3) | 0.009 (3) |
| C6 | 0.050 (4) | 0.046 (4) | 0.045 (4) | -0.003 (3) | -0.003 (3) | -0.002 (3) |
| C7 | 0.052 (4) | 0.042 (4) | 0.035 (3) | 0.007 (3) | -0.004 (3) | 0.000 (3) |
| C8 | 0.077 (5) | 0.074 (5) | 0.070 (5) | -0.009 (4) | 0.024 (4) | -0.009 (4) |
| C9 | 0.094 (6) | 0.088 (6) | 0.054 (5) | -0.018 (5) | 0.003 (4) | -0.023 (4) |

Geometric parameters (Å, °)

| | | | |
|-----------|-----------|------------|-----------|
| Br1—C4 | 1.885 (6) | C2—H2 | 0.9303 |
| Cl1—C3 | 1.741 (6) | C3—C4 | 1.372 (9) |
| O1—C7 | 1.227 (7) | C4—C5 | 1.390 (9) |
| O2—N2 | 1.417 (6) | C5—C6 | 1.363 (9) |
| O2—C9 | 1.428 (8) | C5—H5 | 0.9302 |
| N1—C7 | 1.356 (8) | C6—H6 | 0.9302 |
| N1—C1 | 1.401 (7) | C8—H8A | 0.9604 |
| N1—H1 | 0.8602 | C8—H8B | 0.9599 |
| N2—C7 | 1.385 (7) | C8—H8C | 0.9601 |
| N2—C8 | 1.452 (9) | C9—H9A | 0.9605 |
| C1—C6 | 1.388 (8) | C9—H9B | 0.9600 |
| C1—C2 | 1.404 (8) | C9—H9C | 0.9602 |
| C2—C3 | 1.372 (8) | | |
| N2—O2—C9 | 108.4 (5) | C6—C5—H5 | 119.9 |
| C7—N1—C1 | 125.4 (5) | C4—C5—H5 | 119.3 |
| C7—N1—H1 | 117.2 | C5—C6—C1 | 121.4 (6) |
| C1—N1—H1 | 117.4 | C5—C6—H6 | 119.6 |
| C7—N2—O2 | 113.5 (5) | C1—C6—H6 | 119.0 |
| C7—N2—C8 | 118.6 (6) | O1—C7—N1 | 124.9 (5) |
| O2—N2—C8 | 112.0 (5) | O1—C7—N2 | 119.5 (6) |
| C6—C1—N1 | 118.7 (5) | N1—C7—N2 | 115.4 (5) |
| C6—C1—C2 | 117.8 (6) | N2—C8—H8A | 109.4 |
| N1—C1—C2 | 123.5 (5) | N2—C8—H8B | 110.0 |
| C3—C2—C1 | 119.9 (6) | H8A—C8—H8B | 109.5 |
| C3—C2—H2 | 120.1 | N2—C8—H8C | 109.0 |
| C1—C2—H2 | 120.0 | H8A—C8—H8C | 109.5 |
| C4—C3—C2 | 121.9 (6) | H8B—C8—H8C | 109.5 |
| C4—C3—Cl1 | 121.1 (5) | O2—C9—H9A | 109.4 |
| C2—C3—Cl1 | 117.0 (5) | O2—C9—H9B | 110.2 |
| C3—C4—C5 | 118.1 (6) | H9A—C9—H9B | 109.5 |
| C3—C4—Br1 | 122.3 (5) | O2—C9—H9C | 108.8 |
| C5—C4—Br1 | 119.6 (5) | H9A—C9—H9C | 109.5 |

| | | | |
|---------------|------------|--------------|------------|
| C6—C5—C4 | 120.8 (6) | H9B—C9—H9C | 109.5 |
| C9—O2—N2—C7 | -124.6 (6) | C3—C4—C5—C6 | -1.1 (9) |
| C9—O2—N2—C8 | 97.8 (7) | Br1—C4—C5—C6 | 178.5 (5) |
| C7—N1—C1—C6 | -157.8 (6) | C4—C5—C6—C1 | -0.1 (9) |
| C7—N1—C1—C2 | 23.3 (9) | N1—C1—C6—C5 | -177.4 (5) |
| C6—C1—C2—C3 | -1.8 (9) | C2—C1—C6—C5 | 1.6 (9) |
| N1—C1—C2—C3 | 177.0 (5) | C1—N1—C7—O1 | 6.7 (10) |
| C1—C2—C3—C4 | 0.7 (9) | C1—N1—C7—N2 | -178.0 (5) |
| C1—C2—C3—Cl1 | -179.4 (5) | O2—N2—C7—O1 | -164.2 (5) |
| C2—C3—C4—C5 | 0.8 (9) | C8—N2—C7—O1 | -29.6 (9) |
| Cl1—C3—C4—C5 | -179.1 (5) | O2—N2—C7—N1 | 20.2 (7) |
| C2—C3—C4—Br1 | -178.8 (5) | C8—N2—C7—N1 | 154.8 (6) |
| Cl1—C3—C4—Br1 | 1.3 (8) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1 \cdots O1 ⁱ | 0.86 | 2.11 | 2.902 (7) | 153 |
| N1—H1 \cdots O2 | 0.86 | 2.18 | 2.573 (6) | 108 |
| C2—H2 \cdots O1 | 0.93 | 2.35 | 2.873 (7) | 115 |

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

Fig. 1

