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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
R factor = 0.071
wR factor = 0.186
Data-to-parameter ratio = 13.0

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

2-(*p*-Bromophenylhydrazono)-3-oxo-butanoic acid

The skeleton, without hydrogen atoms, of the title molecule, $C_{10}H_9BrN_2O_3$, is planar, and intramolecular N—H···O and O—H···O hydrogen bonds contribute to this planarity. The molecules exist in the stereoisomeric Z form.

Comment

As a part of our project to study the crystal structures of a series of phenylhydrazones and their stereochemistry, the crystal structure of the title compound, (I), has been determined.

(I)
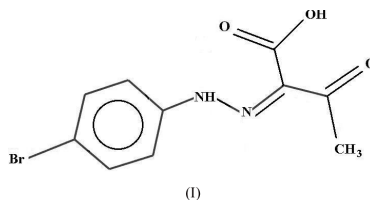
Earlier, this laboratory has reported two related structures, *viz*. 2-(2-methoxyphenylhydrazono)-3-oxobutanoic acid (Rani *et al.*, 2002a) and 3-oxo-2-(phenylhydrazono)butanoic acid (Rani *et al.*, 2002b), compound (I) being a Br derivative of the latter. The replacement of an H atom by a Br atom has effectively increased the volume of the cell by 24.92 Å³ per Br atom. The bond lengths and angles in (I) show normal values and are comparable with those observed in the two reported structures. The molecule is nearly planar, with atoms O1 and C10 displaced from the mean least-squares plane by −0.108 (5) and 0.127 (10) Å, respectively (on opposite sides). The planarity of the molecule is facilitated by the intramolecular hydrogen bonds. The N1—H1N bond is involved in the formation of a bifurcated hydrogen bond; the shorter interaction, called the major component (Steiner, 2002), is an intramolecular N1—H1N···O2 hydrogen bond with the carbonyl O atom of the carboxyl group, whereas the longer one, the minor component, is an intermolecular N1—H1N···O2(−x, 1 − y, 1 − z) hydrogen bond, pairs of which link two molecules across a centre of symmetry (Table 3). The carbonyl O atom of the carbomethoxy group is also involved in an intramolecular O1—H1O···O3 hydrogen bond with the carboxyl group (Fig. 1). Along the b axis, the molecules related by inversion are stacked alternately 3.419 (5) and 3.490 (5) Å apart, optimum distances for π–π stacking interactions. The short contacts observed in the structure are listed in Table 2. The distance O2···O2(−x, 1 − y, 1 − z) of 2.888 (8) Å is less than the sum of the van der Waals radii, but, since the C8—O2 bond length is 1.217 (9) Å, O2 is the double-bonded

carbonyl O atom, hence the O2$\cdots$O2 contact must be regarded as a strong van der Waals interaction.

Experimental

The title compound, (I), was prepared by the partial hydrolysis of ethyl 2-(2-bromophenylhydrazono)-3-oxobutyrate by the action of strong acids (Prasad *et al.*, 1994) and was recrystallized from methanol at room temperature.

Crystal data

$C_{10}H_9BrN_2O_3$	$Z = 2$
$M_r = 285.10$	$D_x = 1.743$ Mg m^{-3}
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 7.058$ (4) Å	Cell parameters from 25
$b = 7.126$ (3) Å	reflections
$c = 11.311$ (6) Å	$\theta = 17.7–39.9°$
$\alpha = 77.05$ (3)°	$\mu = 5.14$ mm^{-1}
$\beta = 86.35$ (4)°	$T = 293$ (2) K
$\gamma = 78.47$ (5)°	Elongated plate, light yellow
$V = 543.1$ (5) Å^3	$0.25 \times 0.19 \times 0.13$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.026$
ω–2θ scans	$\theta_{max} = 69.9°$
Absorption correction: ψ scan	$h = 0 \rightarrow 8$
(North *et al.*, 1968)	$k = -8 \rightarrow 8$
$T_{min} = 0.756$, $T_{max} = 0.989$	$l = -11 \rightarrow 11$
2079 measured reflections	3 standard reflections
1912 independent reflections	frequency: 60 min
1171 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1211P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.186$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.90$	$\Delta\rho_{max} = 1.11$ e Å^{-3}
1912 reflections	$\Delta\rho_{min} = -0.91$ e Å^{-3}
147 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0018 (11)

Table 1
Selected geometric parameters (Å, °).

|			
Br—C4	1.901 (7)	N1—C1	1.414 (9)
O1—C8	1.330 (9)	N2—C7	1.302 (9)
O2—C8	1.217 (9)	C7—C9	1.462 (10)
O3—C9	1.233 (9)	C7—C8	1.502 (12)
N1—N2	1.302 (8)	C9—C10	1.487 (12)
N2—N1—C1	119.2 (7)	C9—C7—C8	120.6 (7)
C7—N2—N1	122.5 (7)	O2—C8—O1	120.3 (8)
C2—C1—N1	118.8 (8)	O2—C8—C7	122.1 (7)
C6—C1—N1	120.4 (7)	O1—C8—C7	117.6 (7)
C3—C4—Br	120.0 (5)	O3—C9—C7	120.7 (8)
C5—C4—Br	119.2 (6)	O3—C9—C10	121.3 (7)
N2—C7—C9	115.8 (8)	C7—C9—C10	118.0 (8)
N2—C7—C8	123.6 (6)		
C1—N1—N2—C7	−179.7 (6)	N2—C7—C8—O2	4.0 (11)
N2—N1—C1—C2	177.3 (6)	C9—C7—C8—O2	−175.3 (7)
N2—N1—C1—C6	−5.2 (9)	N2—C7—C8—O1	−174.7 (6)
N1—C1—C2—C3	179.4 (6)	N2—C7—C9—O3	176.4 (6)
N1—C1—C6—C5	−179.7 (6)	N2—C7—C9—C10	−2.4 (10)
N1—N2—C7—C9	−179.5 (6)	C8—C7—C9—C10	176.9 (7)
N1—N2—C7—C8	1.2 (10)		
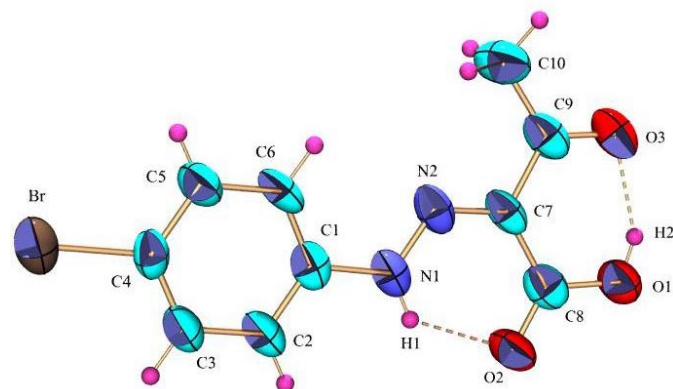
Figure 1
An *ORTEP*-3 plot (Farrugia, 1997) of the title molecule, with 50% probability displacement ellipsoids for non-H atoms. Intramolecular hydrogen bonds are shown as dashed lines.

Table 2
Short intermolecular contacts (Å).

Br$\cdots$O1^i	3.547 (6)	N1$\cdots$C6^i	3.461 (9)
Br$\cdots$O3^{ii}	3.513 (7)	N2$\cdots$C1^i	3.459 (9)
O1$\cdots$C2^{iii}	3.413 (10)	N2$\cdots$C4^v	3.550 (9)
O1$\cdots$C10^{iv}	3.358 (11)	C3$\cdots$C9^i	3.491 (11)
O2$\cdots$O2^{iii}	2.888 (8)	C4$\cdots$C7^v	3.569 (10)
O2$\cdots$C2^{iii}	3.469 (10)	C5$\cdots$C8^i	3.406 (11)
O2$\cdots$C6^{iv}	3.558 (10)		

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

Table 3
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
N1—H1N$\cdots$O2	0.86	2.01	2.656 (9)	131
N1—H1N$\cdots$O2^{iii}	0.86	2.53	3.252 (9)	142
O1—H1O$\cdots$O3	0.82	1.81	2.555 (8)	150

Symmetry code: (iii) $-x, 1-y, 1-z$.

After checking their presence in a difference map, all the H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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organic papers

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