

2-(2-Methoxyphenylhydrazono)-3-oxobutanoic acid

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.046
wR factor = 0.122
Data-to-parameter ratio = 12.8

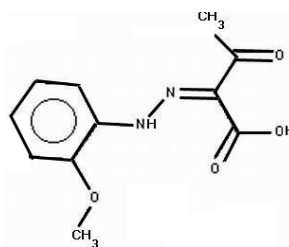
For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal structure of the title compound, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_4$, contains two crystallographically independent molecules in the asymmetric unit. The molecules exist in the stereoisomeric Z form, with the NH group forming an intramolecular N—H···O hydrogen bond with the carbonyl O atom of the carboxyl group. It is also confirmed that the compound exists in the hydrazone form and not the azo form.

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Comment

As 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. These compounds can exist either in the normal hydrazone form ($\text{Ph}-\text{NH}-\text{N}=\text{C}<$) or in the azo form ($\text{Ph}-\text{N}=\text{NH}-\text{CH}<$) and have been extensively investigated by various workers, using both chemical and a range of instrumental methods (Prasad & Sahay, 1993).



(I)

The asymmetric unit of (I) contains two molecules; the corresponding bond lengths and angles of these two molecules agree with each other. The superposition of the non-H atoms of these two molecules (one molecule inverted) resulted in an r.m.s. deviation of 0.04 Å. The $\text{C6}-\text{C1}-\text{N1}-\text{N2}$ [$-7.6(3)^\circ$] and $\text{C6}'-\text{C1}'-\text{N1}'-\text{N2}'$ [$5.4(3)^\circ$] torsion angle values show that these two molecules are slightly distorted from planarity. The structure determination shows that both molecules exist in the stereoisomeric Z form, with the NH group forming an intramolecular N—H···O hydrogen bond with the carbonyl O atom of the carboxyl group (Fig. 1). The carbonyl O atom of the carbomethoxy group is involved in an intramolecular O—H···O hydrogen bond with the carboxyl group (Table 2). In the crystal structure, the inversion-related pairs of the molecules are stacked along [121].

Experimental

The title compound, supplied by Dr N. Prasad, Department of Chemistry, B. R. Ambedkar University, Muzaffarpur, India, was prepared by partial hydrolysis of ethyl 2-(2-methoxyphenylhydrazono)-3-oxobutyrates by the action of strong acids (Prasad *et al.*, 1994) and was recrystallized from methanol at room temperature.

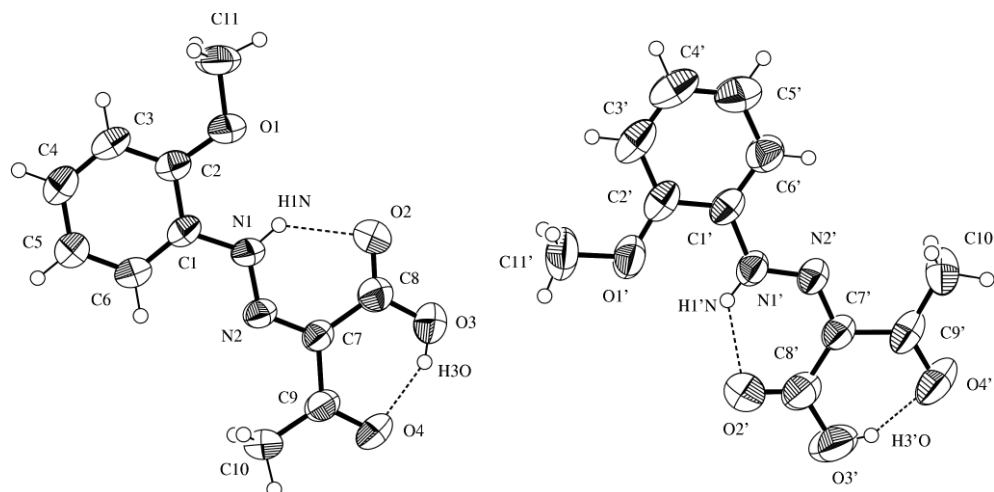


Figure 1

A plot (Farrugia, 1997) of the asymmetric unit of (I), with 50% probability displacement ellipsoids.

Crystal data

$C_{11}H_{12}N_2O_4$
 $M_r = 236.23$
 Triclinic, $P\bar{1}$
 $a = 8.105$ (3) Å
 $b = 11.065$ (2) Å
 $c = 14.163$ (4) Å
 $\alpha = 111.17$ (3)°
 $\beta = 95.85$ (4)°
 $\gamma = 102.97$ (3)°
 $V = 1130.6$ (6) Å³

$Z = 4$
 $D_x = 1.388$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 8.4$ – 11.0 °
 $\mu = 0.11$ mm⁻¹
 $T = 293$ (2) K
 Elongated plate, clear light yellow
 $0.33 \times 0.25 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: none
 4142 measured reflections
 3962 independent reflections
 2114 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.042$

$\theta_{max} = 25.0$ °
 $h = 0 \rightarrow 9$
 $k = -13 \rightarrow 12$
 $l = -16 \rightarrow 16$
 3 standard reflections every 50 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.122$
 $S = 0.88$
 3962 reflections
 309 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0719P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.18$ e Å⁻³
 $\Delta\rho_{min} = -0.13$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O2—C8	1.216 (3)	O2'—C8'	1.209 (3)
O3—C8	1.311 (3)	O3'—C8'	1.319 (3)
O4—C9	1.234 (2)	O4'—C9'	1.228 (3)
N1—N2	1.302 (2)	N1'—N2'	1.299 (2)
N1—C1	1.406 (2)	N1'—C1'	1.409 (3)
N2—C7	1.310 (2)	N2'—C7'	1.308 (3)
C7—C9	1.465 (3)	C7'—C9'	1.464 (3)
C7—C8	1.481 (3)	C7'—C8'	1.473 (3)
N2—N1—C1—C6	−7.6 (3)	N2'—N1'—C1'—C6'	5.4 (3)
C11—O1—C2—C3	−2.4 (3)	C11'—O1'—C2'—C3'	−1.0 (3)

Table 2

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	1.98	2.628 (2)	132
O3—H3O \cdots O4	0.82	1.80	2.554 (2)	152
N1'—H1'N \cdots O2'	0.86	1.98	2.633 (3)	132
O3'—H3'O \cdots O4'	0.82	1.79	2.544 (3)	152

After location in a difference map, all the H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms, using *SHELXL97* (Sheldrick, 1997) defaults.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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References

- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
 Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Prasad, N. & Sahay, A. (1993). *Asian J. Chem. Rev.* **4**, 23–32.
 Prasad, N., Prasad, R. M., Sahay, A., Srivastava, A. K. & Prasad, J. (1994). *Asian J. Chem.* **6**, 901–910.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.