

4-Phenylbutan-2-one semicarbazone

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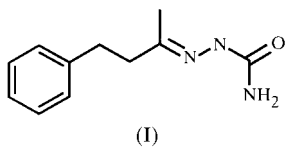
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The title compound, $C_{11}H_{15}N_3O$, crystallizes with two molecules in the asymmetric unit, which are held together by an extended network of hydrogen bonds. It is remarkable that only five of the six theoretically possible hydrogen bonds are formed.

Comment

The semicarbazone moiety is found very often in molecules complexing different metal atoms (Palenik *et al.*, 1976; Palenik & Wester, 1978). Since the complexing atoms are the carbonyl O atom and the imine N atom, the conformation of the $O=C-N-N$ fragment is *cis*. However, the free semicarbazone moiety prefers the *trans* conformation of the $O=C-N-N$ fragment; of 67 fragments retrieved from the Cambridge Structural Database (Version 5.18 of October 1999; Allen & Kennard, 1993), only seven display a *cis* conformation of the fragment in question. Bond lengths and angles do not show remarkable differences between complexing and non-complexing semicarbazone moieties. The phenylethyl moiety of one of the two molecules in the asymmetric unit is disordered. The reason for this disorder is differences in the torsion angles about the bonds $C1-C11$, $C1A-C11A$ and $C1B-C11B$, and about $C2-C3$, $C2A-C3$ and $C2B-C3$. The torsion angle about the CH_2-CH_2 bond is *trans* in all three conformations.



A remarkable feature of the title compound, (I), is that only five of the six possible hydrogen bonds are formed. While the two carbonyl O atoms act as an acceptor for two hydrogen

bonds each, only one of the imine N atoms is involved in a hydrogen bond. The closest H atom to N4A ($N \cdots H$ 2.774 Å) is H4Cⁱ [symmetry code: (i) $x, y - 1, z$], one of the methyl H atoms of C4.

Experimental

To a stirred solution of 150 ml warm sodium ethylate (500 mmol sodium) and 63.16 ml (500 mmol) acetoacetic ester 60 ml freshly distilled (0.52 mmol), benzyl chloride was added dropwise. The mixture was refluxed for 16 h. For work-up, the ethanol was distilled off. The solid residue was dissolved in 100 ml water containing 50 g ice. The solution was extracted three times with diethyl ether and the organic phase was dried with sodium sulfate. After removing the solvent, the crude 2-benzyl acetoacetic ester was purified by fractional distillation. In the second reaction step, 22.0 g (100 mmol) of 2-benzyl acetoacetic ester and 11.22 g (200 mmol) potassium hydroxide in 100 ml absolute ethanol were boiled to reflux for 14 h. The mixture was hydrolyzed in 300 ml iced water containing 5 ml concentrated sulfuric acid. The solution was extracted four times with diethyl ether. The organic phase was washed with water and dried over sodium sulfate. 4-Phenyl-2-butanone was purified by fractional distillation under vacuum. In the last step, 5 g (45 mmol) semicarbazide hydrochloride and 10 g (122 mmol) sodium acetate in 30 ml water was added to 2 g (13 mmol) 4-phenyl-2-butanone in 30 ml ethanol. The crude product was collected by filtration. Recrystallization from acetone yielded crystals suitable for X-ray diffraction.

Crystal data

$C_{11}H_{15}N_3O$	$D_x = 1.206 \text{ Mg m}^{-3}$
$M_r = 205.26$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 508 reflections
$a = 14.059(1) \text{ \AA}$	$\theta = 1-25^\circ$
$b = 7.1282(9) \text{ \AA}$	$\mu = 0.080 \text{ mm}^{-1}$
$c = 22.621(2) \text{ \AA}$	$T = 173(2) \text{ K}$
$\beta = 94.148(1)^\circ$	Plate, colourless
$V = 2261.0(4) \text{ \AA}^3$	$0.72 \times 0.58 \times 0.12 \text{ mm}$
$Z = 8$	

Data collection

Siemens CCD three-circle diffractometer	$R_{\text{int}} = 0.038$
ω scans	$\theta_{\text{max}} = 27.48^\circ$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$h = -17 \rightarrow 18$
$T_{\text{min}} = 0.944$, $T_{\text{max}} = 0.990$	$k = -8 \rightarrow 9$
33 568 measured reflections	$l = -29 \rightarrow 28$
5099 independent reflections	443 standard reflections
4035 reflections with $I > 2\sigma(I)$	frequency: 1080 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.8063P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.065$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
5099 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
371 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0044 (6)

Table 1

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N5—H5 \cdots O6A	0.872 (17)	2.153 (17)	3.0163 (14)	170.3 (15)
N6—H6A \cdots O6 ⁱ	0.861 (18)	2.331 (18)	3.0881 (16)	146.9 (15)
N6—H6B \cdots N4 ⁱⁱ	0.874 (17)	2.262 (17)	3.1273 (17)	170.2 (14)
N5A—H5A \cdots O6	0.877 (17)	2.089 (18)	2.9492 (15)	166.8 (14)
N6A—H6D \cdots O6A ⁱⁱⁱ	0.917 (19)	2.01 (2)	2.9265 (16)	176.6 (16)

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

All H atoms were initially located by difference Fourier synthesis. Subsequently the positions of those bonded to C atoms were idealized and constrained to ride on their parent atoms with C—H(aromatic) = 0.95 Å or C—H(methyl) = 0.98 Å, and fixed individual displacement parameters [$U(H) = 1.2U_{eq}(\text{aromatic C})$ or $1.5U_{eq}(\text{methyl C})$]. The methyl groups were allowed to rotate about

their local threefold axes. H atoms bonded to N were refined isotropically.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

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