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Intermolecular Hydrogen-Bonded Structure of (1*R*)-(+)-Camphor Semicarbazone

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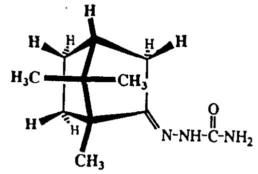
Abstract

The first crystal structure of a rigid asymmetric semicarbazone, $C_{11}H_{19}N_3O$ {hydrazinecarboxamide, (1*R*)-(+)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylene-}, is described. [For a discussion of CAS/IUPAC nomenclature of semicarbazones see Grasselli & Weast (1989). *Handbook of Data on Organic Compounds*, 2nd ed., Vol. I, Introduction, §§190, 252. Boca Raton, Florida: CRC Press.] Crystalline (1*R*)-(+)-camphor semicarbazone (I) was found to have a fused hydrogen-bonded polymeric non-centrosymmetric structure. In each monomeric unit of (I), the hydrazidic H atom and one amidic H atom are *syn* to the carbonyl O atom; these atoms are involved in the intermolecular hydrogen bonding. The carbonyl O atom of each molecule is hydrogen bonded to the hydrazidic H atom of an adjacent molecule and the *syn*-amidic H atom of a different adjacent molecule to form a chain of fused eight-membered rings, the conformation of each ring being distorted from planarity. The hydrazidic hydrogen-bond geometry is N—H = 0.83 (4), H···O = 2.31 (4), N···O = 3.137 (4) Å and N—H···O = 177 (4)°. For the amidic hydrogen bond, N—H = 0.90 (4), H···O = 2.05 (4), N···O = 2.933 (4) Å and N—H···O = 167 (4)°.

Comment

The abnormally high IR C=O frequencies exhibited by semicarbazones in the solid state, investigated by correlating a combination of Raman spectroscopic and X-ray crystallographic data, have been traced to vibrational coupling of C=O in the solid-state hydrogen-bonded network (Kolb, Dantzman, Kozenski & Strommen, 1993; see also discussion in Kolb, Robinson & Meyers, 1994). In that study, the X-ray crystal structures of 14 aliphatic and aromatic aldehyde and ketone semicarbazones typically showed a pattern of polymeric intermolecularly hydrogen-bonded fused eight-membered rings (Kolb, Stupar, Janota & Duax, 1989; Naik & Palenik, 1974; Etter, Britton & Videnova-Adrabinska, 1990; Pangborn, Galitsky, Duax & Kolb, 1991). In this context we chose next to examine (1*R*)-(+)-camphor semicarbazone (I), whose atypical rigid-bicyclic asymmetric molecular structure might give rise to a different hydrogen-bonding pattern. No X-ray structure of a rigid asymmetric semicarbazone had been reported prior to our initial report of these results (Kolb, Meyers & Robinson, 1993).



(I)

The preparation of (1*R*)-(+)-camphor semicarbazone (I) from the reaction of (1*R*)-(+)-camphor with semicarbazide (Kolb, Stupar, Janota & Duax, 1989) provided colorless crystals (from ethanol-water), m.p. 510-515 K (uncorrected). The structure of a monomeric unit is shown in Fig. 1.

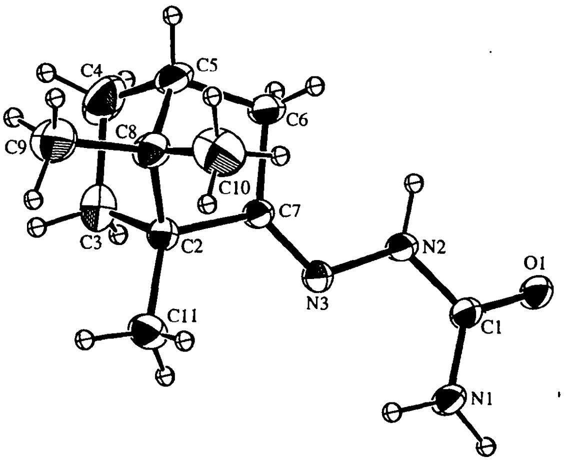


Fig. 1. Molecular configuration and atom-numbering scheme with displacement ellipsoids at the 30% probability level. H atoms are shown as unlabeled isotropic spheres of arbitrary radii.

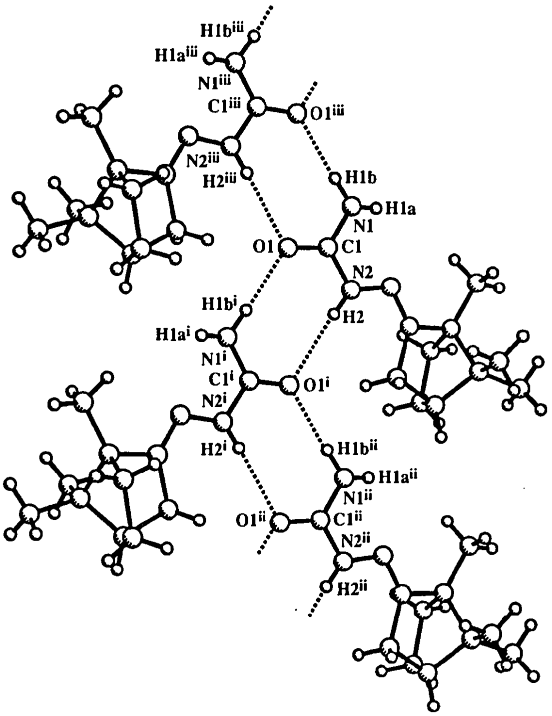


Fig. 2. Polymeric hydrogen bonding of (I). Crystallographically equivalent atoms in different asymmetric units are designated by the superscripts (i), (ii) and (iii) as defined in Table 2.

Fig. 2 shows the polymeric intermolecular hydrogen bonding; the geometric hydrogen-bonding parameters and the definition of symmetry codes (i), (ii) and (iii) are included in Table 2. In each monomeric unit, the hydrazidic H atom (H2) and one amidic H atom (H1*b*) are *syn* to their carbonyl O atom (O1); these atoms are involved in the intermolecular hydrogen bonding while the *anti*-amidic H atom (H1*a*) is not. The carbonyl O atom of a molecule is hydrogen-bonded to H2 of an adjacent molecule and H1*b* of another adjacent molecule to form fused eight-membered-ring intermolecular bridges. The two types of hydrogen bonds, *i.e.* hydrazidic ($N2^{iii}—H2^{iii}\cdots O1$) and amidic ($N1^{i}—H1b^{i}\cdots O1$) are crystallographically distinct. The eight-membered rings are themselves distorted from planarity and they form a slightly corrugated zigzag chain with a zigzag angle, $N1^{i}\cdots O1\cdots N2^{iii}$, of 115.6 (1)°.

The intermolecular hydrogen-bonding patterns of the crystalline semicarbazone (I), bis(*p*-methoxybenzaldehyde) carbazone, and bis(*m*-fluorobenzaldehyde) carbazone are distinctly different from each other (Kolb, Meyers & Robinson, 1993).

Experimental

Crystal data

$C_{11}H_{19}N_3O$
$M_r = 209.29$
Orthorhombic
$P2_12_12_1$
$a = 11.203\ (5)$ Å
$b = 14.206\ (3)$ Å
$c = 7.410\ (1)$ Å
$V = 1179.2\ (6)$ Å^3
$Z = 4$
$D_x = 1.179$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.0–17.3°$
$\mu = 0.073$ mm^{-1}
$T = 296$ K
Prism
0.38 × 0.26 × 0.20 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1236 measured reflections
1236 independent reflections
801 observed reflections
$[I > 3.0\sigma(I)]$

$\theta_{max} = 25°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 100 reflections
intensity variation: -0.1%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.042$
$S = 1.53$
801 reflections
145 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.12$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)
Absolute configuration: correct enantiomer chosen on the basis of the known absolute configuration of the (1*R*)-(+)-camphor used in the synthesis

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.2446 (2)	−0.0243 (2)	1.1978 (3)	0.051 (1)
N1	0.3966 (3)	0.0312 (3)	1.3647 (4)	0.057 (1)
N2	0.4005 (3)	0.0451 (2)	1.0575 (4)	0.045 (1)
N3	0.4990 (2)	0.1034 (2)	1.0781 (4)	0.040 (1)
C1	0.3418 (3)	0.0156 (3)	1.2086 (5)	0.041 (1)
C2	0.6551 (3)	0.1980 (3)	0.9340 (5)	0.045 (1)
C3	0.6079 (4)	0.2902 (3)	0.8520 (6)	0.071 (1)
C4	0.5861 (5)	0.2653 (4)	0.6511 (6)	0.091 (2)
C5	0.6188 (4)	0.1620 (4)	0.6419 (5)	0.067 (1)
C6	0.5207 (3)	0.1095 (3)	0.7398 (5)	0.056 (1)
C7	0.5485 (3)	0.1328 (2)	0.9341 (4)	0.038 (1)
C8	0.7254 (3)	0.1553 (3)	0.7731 (5)	0.055 (1)
C9	0.8338 (4)	0.2136 (4)	0.7150 (6)	0.091 (2)
C10	0.7682 (4)	0.0551 (4)	0.8100 (7)	0.086 (2)
C11	0.7170 (4)	0.2108 (3)	1.1121 (5)	0.063 (1)
H1*a*	0.457 (3)	0.071 (3)	1.366 (6)	0.068
H1*b*	0.354 (3)	0.019 (3)	1.465 (5)	0.068
H2	0.360 (3)	0.038 (3)	0.965 (5)	0.054

Table 2. *Selected geometric parameters* (Å, °)

O1—C1	1.229 (4)	C3—C4	1.550 (6)
N1—C1	1.328 (4)	C4—C5	1.514 (7)
N2—N3	1.388 (4)	C5—C6	1.514 (5)
N2—C1	1.365 (4)	C5—C8	1.543 (6)
N3—C7	1.273 (4)	C6—C7	1.510 (5)

C2—C3	1.537 (6)	C8—C9	1.531 (5)
C2—C7	1.511 (4)	C8—C10	1.527 (6)
C2—C8	1.553 (5)	N1—H1*a*	0.89 (4)
C2—C11	1.502 (5)		
N3—N2—C1	118.5 (3)	C4—C5—C6	106.3 (4)
N2—N3—C7	116.8 (3)	C4—C5—C8	102.6 (4)
O1—C1—N1	122.9 (3)	C6—C5—C8	103.3 (3)
O1—C1—N2	121.0 (3)	C5—C6—C7	101.5 (3)
N1—C1—N2	116.1 (3)	N3—C7—C2	123.1 (3)
C3—C2—C7	104.5 (3)	N3—C7—C6	129.5 (3)
C3—C2—C8	101.8 (3)	C2—C7—C6	107.3 (3)
C3—C2—C11	113.8 (3)	C2—C8—C5	93.8 (3)
C7—C2—C8	99.3 (3)	C2—C8—C9	114.1 (4)
C7—C2—C11	116.0 (3)	C2—C8—C10	112.7 (3)
C8—C2—C11	119.2 (3)	C5—C8—C9	113.8 (3)
C2—C3—C4	103.8 (4)	C5—C8—C10	114.4 (4)
C3—C4—C5	103.1 (4)	C9—C8—C10	107.8 (4)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*b*···O1^{iii}	0.90 (4)	2.05 (4)	2.933 (4)	167 (4)
N2—H2···O1^{i}	0.83 (4)	2.31 (4)	3.137 (4)	177 (4)

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

The scan rate was 6° $\min^{-1}$ (in ω). Weak reflections [$I < 10\sigma(I)$] were rescanned (maximum of three rescans) and the counts accumulated to improve accuracy. The positional parameters of atoms H1*a*, H1*b* and H2 were refined; all other H atoms were placed at assumed positions (C,N—H = 0.95 Å, $U = 1.2 \times U_{eq}$ of associated C atom) and fixed. Data Collection *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN, ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71746 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1088]

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3-β-D-Ribofuranosyl-6,7-dihydro-9*H*-thiazolo[3,2-*a*]purin-9-one Hydrate

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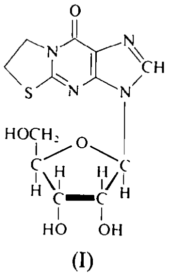
Abstract

The title molecule, $C_{12}H_{14}N_4O_5S.H_2O$ (I), has a *syn*-χ_{CN} glycosyl torsion angle, which is stabilized by an intramolecular hydrogen bond between N3 of the tricylic base and O5′ of the ribose (in a C2′-*endo* pucker). [The purine base, including atoms S and O6, of the molecule is planar to within 0.043 (2) Å.] The tricyclic bases are stacked along *a* with an interplanar distance of 3.602 (3) Å.

Comment

As part of anti-tumour drug research, the structure of (I) has been determined in order to elucidate the sugar pucker and glycosyl torsion conformations. Details of the synthetic work have been published elsewhere (Chern, Lin & Chen, 1990).



(I)

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