

## 1-Hydroxy-cis-bicyclo[5.3.0]dec-9-en-8-one

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**Abstract.**  $C_{10}H_{14}O_2$ ,  $M_r = 166.2$ , monoclinic,  $P2_1/c$ ,  $a = 12.526$  (4),  $b = 6.605$  (1),  $c = 10.686$  (2) Å,  $\beta = 95.88$  (2)°,  $V = 879.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.25$  (–35°C),  $D_m = 1.24$  (22°C) g cm<sup>–3</sup>. Full-matrix least-squares refinement yielded a final  $R$  of 0.050 using the 1199 reflections [ $I_o \geq 2.0\sigma(I_o)$ ] collected at –35°C on a Syntex  $P2_1$  diffractometer. The five-membered ring is only slightly puckered, and the seven-membered ring is in a distorted chair conformation. Intermolecular hydrogen bonding occurs between the hydroxyl H and the carbonyl O.

**Introduction.** The title compound crystallizes as clear rectangular plates. Preliminary X-ray diffraction experiments using a Syntex  $P2_1$  automated diffractometer showed the crystal system to be monoclinic. The systematically absent reflections indicated that the space group was  $P2_1/c$ . Intensity-data collection information is given in Table 1. Lorentz and polarization corrections were applied to the intensity data. Corrections for crystal decay or absorption were not required. Data-reduction procedures and principal computer programs used in this study are as detailed earlier (Riley & Davis, 1976). A  $p$  factor of 0.02 was used in estimating the standard deviations in intensities.

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Table 1. Experimental summary for  $C_{10}H_{14}O_2$ 

Syntex  $P2_1$  autodiffractometer equipped with graphite monochromator and Syntex LT-1 low-temperature flow system  
Radiation: Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å  
Mode:  $\omega$ -scan technique, recentered automatically after every 700 reflections  
Scan range: symmetrically over 1.0° about the  $K\alpha_{1,2}$  maximum  
Scan rate: variable, 1.5 to 5.0° min<sup>–1</sup>  
Background: offset 1.0° and –1.0° in  $\omega$  from the  $K\alpha_{1,2}$  maximum  
Check reflections: four remeasured after every 96 reflections; analysis\* of 25 sets of check reflections indicated that a decay correction was not required  
2020 independent reflections measured in octants  $hkl$  and  $h\bar{k}l$ ;  $4^\circ \leq 2\theta \leq 55^\circ$   
Data-crystal dimensions: approx. 0.45 × 0.30 × 0.20 mm  
Absorption coefficient:  $\mu(\text{Mo } K\alpha) = 0.925$  cm<sup>–1</sup>. No absorption correction applied

\* Henslee &amp; Davis (1975).

The structure was solved using the direct-methods program *MULTAN* (Main, Woolfson & Germain, 1971). Anisotropic full-matrix least-squares refinement [2020 reflections,  $I_o \geq 2\sigma(I_o)$ ] of the positional and thermal parameters of the non-hydrogen atoms gave  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.102$  and  $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.121$ , where  $w = 1/\sigma^2(|F_o|)$ . Probable coordinates for the H atoms were calculated and their positions were verified in a difference map. Subsequent isotropic refinement of the H atoms with anisotropic refinement of the nonhydrogen atoms gave a final  $R = 0.050$  and  $R_w = 0.041$ .† The calculated

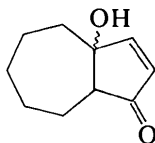
† Lists of structure factors, nonhydrogen atom anisotropic thermal parameters and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32906 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Atomic parameters for  $C_{10}H_{14}O_2$  with e.s.d.'s in parenthesesAtomic fractional coordinates for C and O atoms are  $\times 10^4$ ; those for H atoms are  $\times 10^3$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
O(1)	8957 (1)	5879 (3)	884 (2)	
O(2)	8671 (1)	12305 (3)	–587 (2)	
C(1)	8248 (2)	8815 (3)	–299 (2)	
C(2)	8795 (2)	7696 (3)	834 (2)	
C(3)	9052 (2)	9160 (4)	1840 (2)	
C(4)	8665 (2)	10947 (4)	1495 (2)	
C(5)	8100 (2)	10995 (3)	176 (2)	
C(6)	6947 (2)	11732 (4)	193 (2)	
C(7)	6321 (3)	12096 (5)	–1093 (3)	
C(8)	5872 (2)	10220 (5)	–1771 (3)	
C(9)	6693 (2)	8658 (4)	–2060 (2)	
C(10)	7279 (2)	7655 (4)	–901 (2)	
H(O)	875 (2)	1344 (5)	–24 (3)	5.9 (8)
H(1)	874 (2)	888 (3)	–93 (2)	2.9 (5)
H(3)	946 (2)	879 (3)	261 (2)	3.2 (5)
H(4)	870 (2)	1218 (3)	201 (2)	3.1 (5)
H(6A)	658 (2)	1070 (4)	72 (2)	3.9 (6)
H(6B)	697 (2)	1299 (3)	66 (2)	2.8 (5)
H(7A)	571 (2)	1296 (4)	–95 (2)	5.4 (7)
H(7B)	677 (2)	1285 (4)	–160 (3)	5.6 (8)
H(8A)	534 (2)	962 (4)	–129 (2)	4.5 (7)
H(8B)	546 (2)	1064 (4)	–256 (2)	4.4 (6)
H(9A)	632 (2)	761 (3)	–259 (2)	3.5 (5)
H(9B)	722 (2)	925 (4)	–260 (2)	3.8 (6)
H(10A)	680 (2)	744 (4)	–23 (2)	3.5 (5)
H(10B)	757 (2)	625 (4)	–113 (2)	3.1 (5)

maximum residual electron density was  $0.17 \text{ e } \text{Å}^{-3}$ . Of the non-hydrogen atomic parameters, none shifted by more than 0.02 of its e.s.d. Atomic scattering factors for C and O were taken from *International Tables for X-ray Crystallography* (1974). H atom scattering factors were taken from Stewart, Davidson & Simpson (1965). Atomic parameters are given in Table 2.

**Discussion.** In a study of reactions involving addition of nitro-olefins to di- and trianions of 1,3-diketones, followed by cyclization, Ehrig & Seebach (1975) obtained bicyclic hydroxyketones. The single-crystal X-ray diffraction study of the title compound



was undertaken to determine the stereochemistry at the ring junction.

A stereoview of the molecule is given in Fig. 1, showing that the ring fusion has the *cis* stereochemistry. Bond lengths and bond angles appear in Table 3. The only apparent abnormality in these values is the unusually short C=C double-bond distance,  $C(3)-C(4) = 1.314(3) \text{ Å}$ . This is shorter than the distance,  $1.342(10) \text{ Å}$ , observed in cyclopentene (Davis & Muecke, 1970), whereas it would be expected to be somewhat longer owing to conjugation with the C=O double bond. However, in several pseudoguaianolide derivatives, involving cyclopentenone fused to seven-membered rings, C=C distances shorter than or equal to that in cyclopentene have been observed [bromomexicanin-E,  $1.32(1) \text{ Å}$ , Mazhar-ul-Haque & Caughlan, 1967; bromohelenalin,  $1.31(1) \text{ Å}$ , Mazhar-ul-Haque & Caughlan, 1969; 3-bromoanhydrodehydrodihdropulchellin,  $1.33(1) \text{ Å}$ , Aota, Caughlan, Emerson, Herz, Inayama & Mazhar-ul-Haque, 1970; neophorbol,  $1.34(1) \text{ Å}$ , Brandl, Röhrli, Zechmeister & Hoppe, 1971]. We can offer no explanation for the apparent shortness of this bond.

Table 3. Bond lengths (Å) and bond angles (°) for  $C_{10}H_{14}O_2$

Estimated standard deviations shown in parentheses refer to the last decimal position.

C(1)–C(2)	1.520 (3)	C(5)–C(1)–C(2)	104.5 (2)
C(1)–C(5)	1.545 (3)	C(1)–C(2)–C(3)	108.2 (2)
C(1)–C(10)	1.522 (3)	C(2)–C(3)–C(4)	110.0 (2)
C(2)–C(3)	1.458 (3)	C(3)–C(4)–C(5)	113.8 (2)
C(3)–C(4)	1.314 (3)	C(4)–C(5)–C(1)	103.1 (2)
C(4)–C(5)	1.512 (3)	C(1)–C(5)–C(6)	116.6 (2)
C(5)–C(6)	1.527 (3)	C(5)–C(6)–C(7)	116.0 (2)
C(6)–C(7)	1.530 (4)	C(6)–C(7)–C(8)	115.6 (2)
C(7)–C(8)	1.515 (4)	C(7)–C(8)–C(9)	115.4 (2)
C(8)–C(9)	1.513 (4)	C(8)–C(9)–C(10)	114.3 (2)
C(9)–C(10)	1.525 (4)	C(9)–C(10)–C(1)	114.9 (2)
O(1)–C(2)	1.218 (3)	C(10)–C(1)–C(5)	119.4 (2)
O(2)–C(5)	1.431 (3)	C(10)–C(1)–C(2)	111.6 (2)
		C(4)–C(5)–C(6)	110.4 (2)
		O(1)–C(2)–C(1)	125.0 (2)
		O(1)–C(2)–C(3)	126.8 (2)
		O(2)–C(5)–C(4)	109.3 (2)
		O(2)–C(5)–C(6)	110.1 (2)

Table 4. Non-hydrogen torsion angles (Klyne & Prelog, 1960) for  $C_{10}H_{14}O_2$

O(1)–C(2)–C(1)–C(5)	172.36°
O(1)–C(2)–C(1)–C(10)	41.94
O(1)–C(2)–C(3)–C(4)	–173.55
O(2)–C(5)–C(1)–C(2)	120.05
O(2)–C(5)–C(1)–C(10)	–114.35
O(2)–C(5)–C(4)–C(3)	–115.98
O(2)–C(5)–C(6)–C(7)	52.21
C(1)–C(2)–C(3)–C(4)	4.60
C(1)–C(5)–C(4)–C(3)	–2.41
C(1)–C(5)–C(6)–C(7)	–69.86
C(1)–C(10)–C(9)–C(8)	–84.87
C(2)–C(1)–C(5)–C(4)	4.84
C(2)–C(1)–C(5)–C(6)	–116.30
C(2)–C(1)–C(10)–C(9)	–179.05
C(2)–C(3)–C(4)–C(5)	–1.31
C(3)–C(2)–C(1)–C(5)	–5.83
C(3)–C(2)–C(1)–C(10)	–136.25
C(3)–C(4)–C(5)–C(6)	122.79
C(4)–C(5)–C(1)–C(10)	130.44
C(4)–C(5)–C(6)–C(7)	172.98
C(5)–C(1)–C(10)–C(9)	58.74
C(5)–C(6)–C(7)–C(8)	79.28
C(6)–C(5)–C(1)–C(10)	9.30
C(6)–C(7)–C(8)–C(9)	–60.04
C(7)–C(8)–C(9)–C(10)	66.05

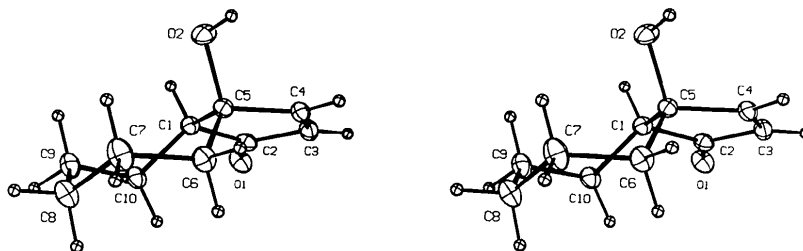


Fig. 1. A stereoview of  $C_{10}H_{14}O_2$  illustrating the atom-numbering scheme. Non-hydrogen atoms are shown as 20% equiprobability ellipsoids; H atoms appear as  $0.10 \text{ Å}$  radius spheres. H atoms are numbered to correspond to the atoms to which they are attached; the hydroxyl H atom is designated H(O). H atoms which are *endo* (i.e. on the opposite side of the fused-ring system from the hydroxyl group) are designated by the suffix A; *exo* H atoms are designated by the suffix B.

Table 5. Intermolecular bond lengths and angles for the hydrogen-bonding system

	Distance (Å)	Expected* van der Waals distance (Å)
O(2)—H(O)	0.84 (3)	
H(O)···O(1)	2.01 (3)	2.72
O(1)···O(2)	2.840 (2)	2.92
		Angle
H(O)—O(2)···O(1)		7.2 (2.0)°
H(O)···O(1)···O(2)		3.0 (0.8)
O(2)—H(O)···O(1)		169.8 (2.8)

\* Van der Waals radii (Bondi, 1964): H: 1.2 Å; O (singly bonded): 1.52 Å; O (carbonyl), where the interaction is parallel to the double bond: 1.40 Å.

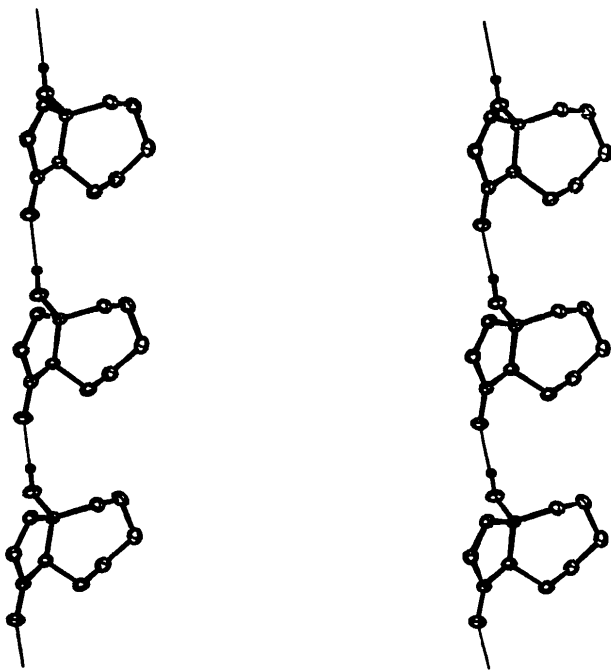


Fig. 2. A stereoview illustrating the hydrogen-bonding scheme between the hydroxyl H and the carbonyl O along the  $y$  direction.

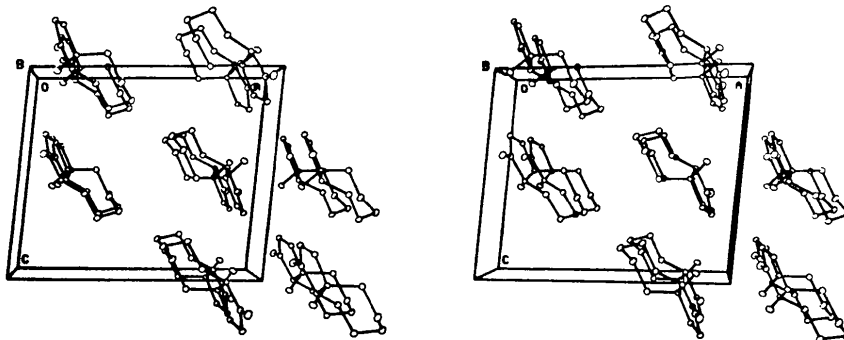


Fig. 3. A stereoview along the  $y$  axis illustrating the packing of the hydrogen-bonded chains of molecules.

The conformations of the two rings are summarized by the torsion angles of Table 4. The five-membered ring is only very slightly puckered (maximum deviation from the best plane of the ring C atoms = 0.035 Å), with the approximate  $C_2$  axis passing through C(4) and the C(1)—C(2) bond. This is in agreement with evidence from microwave spectroscopy that the non-hydrogen skeleton of cyclopent-2-en-1-one is planar (Chadwick, Legon & Millen, 1969). Analysis of the conformations of seven-membered rings on the basis of minimum energetic repulsions of non-bonded interactions has been carried out by Hendrickson (1961) for the four conformation types: chair, boat, twist-chair and twist-boat. The conformation in the present compound is distorted from the idealized chair conformation to what may be described as  $\frac{2}{3}$  chair/ $\frac{1}{3}$  twist-chair.

Consideration of intermolecular distances and angles reveals a hydrogen-bonding scheme between the hydroxyl H on one molecule and the carbonyl O on the neighboring molecule in the  $y$  direction (Table 5). The hydrogen bonding in this string of molecules is illustrated in Fig. 2, while Fig. 3 shows the arrangement of these hydrogen-bonded chains relative to one another.

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### 3-Diazoindazole

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**Abstract.**  $C_7H_4N_4$ , FW 144.1, monoclinic, space group  $P2_1/n$ ,  $a = 6.070$  (1),  $b = 13.140$  (1),  $c = 8.173$  (1) Å,  $\beta = 97.10$  (2)°,  $V = 646.9$  Å<sup>3</sup>,  $D_m = 1.50$  (2) (floatation),  $D_x = 1.480$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 8.316$  cm<sup>-1</sup>,  $Z = 4$ , at 20 (1)°C. The distances in the group  $>C-N-N$  were found to be 1.338 (3) Å for  $>C-N$  and 1.110 (3) Å for  $N-N$ , thus suggesting the carbanionic character  $>C^{\ominus}-N^{\oplus}\equiv N$ . Essentially planar molecules are packed nearly parallel to the  $ac$  plane.

**Introduction.** 3-Diazoindazole (hereinafter DIN) was prepared according to the procedure described by Bamberger (1899). Transparent pale-yellow needles elongated along  $a$  were crystallized from  $n$ -heptane. The systematically absent reflexions ( $0k0$ :  $k = 2n + 1$  and  $h0l$ :  $h + l = 2n + 1$ ) on Weissenberg photographs and the centric distribution of  $|E|$  values ( $\langle E^2 \rangle = 1.000$ ;  $\langle |E^2 - 1| \rangle = 0.996$ ;  $\langle |E| \rangle = 0.795$ ) indicate space group  $P2_1/n$  (No. 14). Unit-cell dimensions were obtained from a least-squares fit of the  $2\theta$  values of 30 reflexions measured on a CAD-4 diffractometer [Cu  $K\alpha_1$  radiation,  $\lambda = 1.54051$  Å,  $t = 20$  (1)°C]. A single crystal with approximate dimensions  $0.2 \times 0.2 \times 0.5$  mm was used for data collection on an automatic computer-controlled Enraf-Nonius CAD-4 four-circle diffractometer with Ni-filtered Cu  $K\alpha$  radiation. Reflexions were scanned in the  $\omega-2\theta$  mode (moving crystal-moving counter) with a variable scan rate. Details of data collection and reduction are shown in Table 1. The compound is sensitive to light and the crystal decayed

in the X-ray beam during the data collection. The data were corrected for variation in reference reflexions and Lorentz-polarization effects. No absorption corrections were made.

The structure was solved by direct methods with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). An  $E$  map with the highest combined figure of merit CFOM (3.000) obtained with the unit weighting of ABSFOM (1.137),  $\psi_0(322)$  and RESID (16.78), computed with 200 phases ( $|E| > 1.40$ ), revealed the positions of all the heavy atoms. The

Table 1. *Data collection summary for DIN*

Temperature (°C)	20 (1)
Diffractometer	CAD-4, automatic, four-circle
Radiation	Cu $K\alpha$ (Ni-filtered) ( $\lambda = 1.5418$ Å)
Scan method	$\omega-2\theta$
$2\theta$ scan width (°)	$0.6 + 0.2 \tan \theta$
Scan rate (° min <sup>-1</sup> )	Minimum: 1.3; maximum: 20.1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{\max}$ (°)	150
Maximum scan time (s)	45
Aperture (mm)	$2.5 + 0.9 \tan \theta$
Reference reflexions	121, 131, 141
Intensity decrease (%)	24.2
Measured reflexions	3560
Averaged reflexions	1328
Mean discrepancy on $I$ (%)	3.1 for 3380 reflexions
Observed reflexions	783
Unobserved reflexions	545 [ $I < 3\sigma(I)$ ]
$\sigma(I)$ base	Counting statistics
Linear absorption coefficient (cm <sup>-1</sup> )	8.316 for Cu $K\alpha$

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