X-Ray Reports for

Synthesis of Cyclic Hydroxamic Acids Through –NOH Insertion of Ketones

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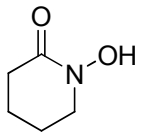
Supporting Information

X-Ray Report for **1**



1

The asymmetric unit contains two $C_5H_9NO_2$ molecules. One of the $C_5H_9NO_2$ molecules shows minor disorder involving two of the ring carbon atoms. All displacement ellipsoids are drawn at the 50% probability level.

Colorless rectangular-parallelepiped-shaped crystals of $C_5H_9NO_2$ are, at 193(2) K, orthorhombic, space group Pbca – D_{2h}^{15} (No. 61)[1] with a = 15.900(3) Å, b = 7.187(1) Å, c = 19.995(4) Å, V = 2284.9(8) Å^3 and Z = 16 molecules {d_{calcd} = 1.339 g/cm^3; μ_a(MoK$\bar{\alpha}$) = .103 mm^{-1}}. A full hemisphere of diffracted intensities (1868 20-second frames with a ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated MoKα radiation (λ= 0.71073 Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System.[2] X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 5101 reflections. A total of 21446 integrated reflection intensities having 2θ((MoK$\bar{\alpha}$)< 58.70° were produced using the Bruker program SAINT;[3] 3116 of these were unique and gave Rint = 0.058 with a coverage which was 99.6% complete. The relative transmission factors ranged from 0.966 to 0.990. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 6.12 software package.[4]

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Hydroxyl hydrogen atoms were located from a difference Fourier map and refined as independent isotropic atoms. The remaining hydrogen atoms were included into the structural model as idealized atoms (assuming sp^3-hybridization of the carbon atoms and C-H bond lengths of 0.99 Å). The isotropic thermal parameters for H_{2O} and H_{4O} refined to final values of 0.069(5) and 0.066(5)Å^2, respectively. The isotropic thermal parameters of the remaining hydrogen atoms were fixed at values 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

One of the two independent molecules shows disorder involving two of the ring carbon atoms with two orientations in the crystal; the major orientation is adopted 71 % of the time and the minor orientation is adopted 29 % of the time. The major (71%) orientation is specified by carbon atoms C_8 and C_9 and hydrogen atoms H_{7A}, H_{7B}, H_{8A}, H_{8B}, H_{9A}, H_{9B}, H_{10A} and H_{10B}; the minor (29%) orientation is specified by carbon atoms $C_{8'}$ and $C_{9'}$ and hydrogen atoms H_{7C}, H_{7D}, $H_{8'A}$, $H_{8'B}$, $H_{9'A}$, $H_{9'B}$, H_{10C} and H_{10D}, respectively.

A total of 172 parameters were refined using no restraints, 3116 data and weights of w = 1/ [$\sigma^2(F^2)$ + (0.0816 P)^2], where P = [F_o^2 + 2F_c^2] / 3. Final agreement factors at convergence are: R_1(unweighted, based on F) = 0.048 for 2332 independent "observed"

reflections having $2\theta(MoK\bar{\alpha}) < 58.70°$ and $I>2\sigma(I)$; R_1(unweighted, based on F) = 0.062 and wR_2(weighted, based on F^2) = 0.130 for all 3116 independent reflections having $2\theta(MoK\bar{\alpha}) < 58.70°$. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.30 and -0.16 $e^-/Å^3$, respectively.

References

(1) International Tables for Crystallography, Vol A, 4th ed., Kluwer: Boston (1996).

(2) Data Collection: SMART Software Version 5.628 (2002). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

(3) Data Reduction: SAINT Software Version 6.36a (2002). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

(4) G. M. Sheldrick (2000). SHELXTL Version 6.12 Reference Manual. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA

Table 1. Crystal data and structure refinement for $C_5H_9NO_2$

Identification code	a52m2m
Empirical formula	C5 H9 N O2
Formula weight	115.13
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca – D_{2h}^{15} (No. 61)
Unit cell dimensions	a = 15.900(3) Å
	b = 7.187(1) Å
	c = 19.995(4) Å
Volume	2284.9(8) $Å^3$
Z	16
Density (calculated)	1.339 g/cm^3
Absorption coefficient	0.103 mm^{-1}
F(000)	992
Crystal size	0.34 x 0.13 x 0.10 mm^3
Theta range for data collection	3.82 to 29.35°
Index ranges	$-20 \le h \le 21$, $-9 \le k \le 9$, $-27 \le l \le 27$
Reflections collected	21446
Independent reflections	3116 [R(int) = 0.0576]
Completeness to theta = 29.35°	99.6 %
Absorption correction	None
Max. and min. transmission	0.9897 and 0.9657
Refinement method	Full-matrix least-squares on F^2
Data / parameters	3116 / 172
Goodness-of-fit on F^2	0.980
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1214
R indices (all data)	R1 = 0.0620, wR2 = 0.1295
Largest diff. peak and hole	0.304 and -0.165 $e^-/Å^3$

$R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR2 = \{ \, \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \, \}^{1/2}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $C_5H_9NO_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	771(1)	-1432(1)	1876(1)	51(1)
O(2)	1634(1)	441(1)	958(1)	42(1)
N(1)	1448(1)	1205(1)	1583(1)	32(1)
C(1)	1045(1)	131(2)	2020(1)	33(1)
C(2)	1867(1)	2964(2)	1714(1)	45(1)
C(3)	1534(1)	3864(2)	2342(1)	58(1)
C(4)	1473(1)	2487(2)	2905(1)	50(1)
C(5)	899(1)	926(2)	2704(1)	44(1)
O(3)	656(1)	1986(1)	69(1)	38(1)
O(4)	-278(1)	3562(1)	-876(1)	45(1)
N(2)	-609(1)	3080(1)	-254(1)	36(1)
C(6)	-95(1)	2329(2)	193(1)	31(1)
C(7)	-1490(1)	3599(2)	-171(1)	47(1)
C(8)	-1727(1)	3574(3)	593(1)	50(1)
C(9)	-1378(1)	1853(4)	925(1)	45(1)
C(10)	-458(1)	1901(2)	872(1)	38(1)
C(8')	-1920(3)	2496(7)	316(2)	40(1)
C(9')	-1411(3)	2866(10)	928(3)	41(1)

Table 3. Bond lengths [Å] and angles [°] for $C_5H_9NO_2$

O(1)-C(1)	1.239(1)	O(3)-C(6)	1.245(1)
O(2)-N(1)	1.397(1)	O(4)-N(2)	1.394(1)
O(2)-H(2O)	0.88(2)	O(4)-H(4O)	0.87(2)
N(1)-C(1)	1.329(2)	N(2)-C(6)	1.325(2)
N(1)-C(2)	1.453(2)	N(2)-C(7)	1.459(2)
C(1)-C(5)	1.501(2)	C(6)-C(10)	1.506(2)
C(2)-C(3)	1.508(2)	C(7)-C(8)	1.572(3)
C(3)-C(4)	1.501(2)	C(8)-C(9)	1.510(3)
C(4)-C(5)	1.502(2)	C(9)-C(10)	1.467(3)
C(7)-C(8')	1.430(5)	C(10)-C(9')	1.670(6)
C(8')-C(9')	1.492(7)		
N(1)-O(2)-H(2O)	106.4(12)	N(2)-O(4)-H(4O)	105.7(12)
C(1)-N(1)-O(2)	117.46(10)	C(6)-N(2)-O(4)	118.00(10)
C(1)-N(1)-C(2)	127.41(10)	C(6)-N(2)-C(7)	128.25(11)
O(2)-N(1)-C(2)	113.98(9)	O(4)-N(2)-C(7)	113.62(10)
O(1)-C(1)-N(1)	122.96(11)	O(3)-C(6)-N(2)	122.47(11)
O(1)-C(1)-C(5)	120.10(11)	O(3)-C(6)-C(10)	120.49(11)
N(1)-C(1)-C(5)	116.90(10)	N(2)-C(6)-C(10)	117.04(11)
N(1)-C(2)-C(3)	111.24(11)	N(2)-C(7)-C(8)	109.75(12)
C(4)-C(3)-C(2)	111.34(13)	C(9)-C(8)-C(7)	110.38(18)
C(3)-C(4)-C(5)	109.32(12)	C(10)-C(9)-C(8)	108.4(2)
C(1)-C(5)-C(4)	115.72(11)	C(9)-C(10)-C(6)	116.85(13)
C(8')-C(7)-N(2)	113.3(2)	C(8')-C(9')-C(10)	111.3(4)
C(7)-C(8')-C(9')	101.5(4)	C(6)-C(10)-C(9')	108.9(2)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_5H_9NO_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	70(1)	38(1)	46(1)	-6(1)	5(1)	-18(1)
O(2)	40(1)	55(1)	30(1)	0(1)	3(1)	10(1)
N(1)	31(1)	36(1)	29(1)	1(1)	1(1)	-1(1)
C(1)	33(1)	31(1)	35(1)	1(1)	0(1)	-2(1)
C(2)	47(1)	38(1)	49(1)	8(1)	1(1)	-11(1)
C(3)	70(1)	36(1)	69(1)	-9(1)	3(1)	-11(1)
C(4)	54(1)	53(1)	43(1)	-14(1)	0(1)	-6(1)
C(5)	55(1)	42(1)	36(1)	-4(1)	9(1)	-8(1)
O(3)	36(1)	42(1)	35(1)	-1(1)	2(1)	1(1)
O(4)	63(1)	41(1)	31(1)	5(1)	-4(1)	-11(1)
N(2)	42(1)	33(1)	33(1)	2(1)	-2(1)	-1(1)
C(6)	37(1)	24(1)	31(1)	-5(1)	-2(1)	-3(1)
C(7)	42(1)	41(1)	59(1)	3(1)	-10(1)	8(1)
C(8)	43(1)	54(1)	53(1)	4(1)	1(1)	19(1)
C(9)	37(1)	49(1)	49(1)	10(1)	5(1)	7(1)
C(10)	42(1)	39(1)	31(1)	-1(1)	2(1)	1(1)
C(8')	33(2)	44(3)	45(3)	-8(2)	-3(2)	-2(2)
C(9')	36(3)	43(3)	44(3)	0(3)	7(2)	9(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_5H_9NO_2$.

	x	y	z	U(eq)
H(2O)	1288(12)	970(30)	672(9)	69(5)
H(2A)	1780	3812	1331	54
H(2B)	2479	2747	1762	54
H(3A)	1911	4895	2475	70
H(3B)	971	4394	2252	70
H(4A)	1251	3109	3310	60
H(4B)	2038	1990	3010	60
H(5A)	957	-90	3035	53
H(5B)	311	1379	2727	53
H(4O)	-458(11)	2720(30)	-1152(8)	66(5)
H(7A)	-1852	2714	-418	57
H(7B)	-1585	4859	-356	57
H(7C)	-1521	4923	-36	57
H(7D)	-1780	3471	-606	57
H(8A)	-1497	4697	814	60
H(8B)	-2347	3596	642	60
H(9A)	-1548	1820	1401	54
H(9B)	-1600	724	703	54
H(10A)	-238	677	1017	45
H(10B)	-245	2843	1191	45
H(10C)	-87	2405	1226	45
H(10D)	-501	537	934	45
H(8'A)	-1912	1160	196	48
H(8'B)	-2510	2908	373	48
H(9'A)	-1707	2359	1324	49
H(9'B)	-1351	4226	991	49

Table 6. Torsion angles [°] for $C_5H_9NO_2$

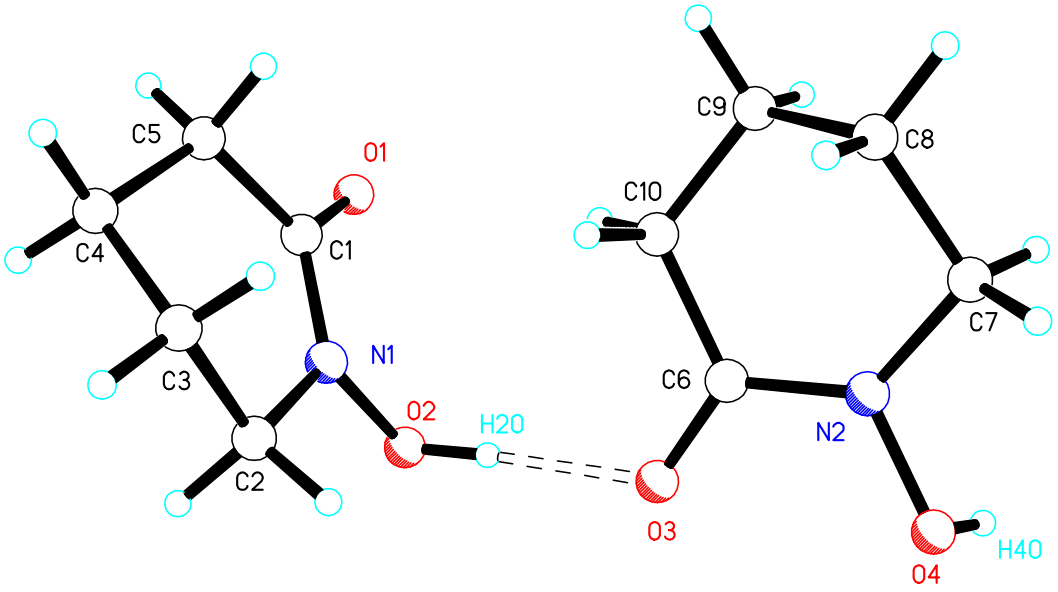
O(2)-N(1)-C(1)-O(1)	-6.27(17)
C(2)-N(1)-C(1)-O(1)	-173.16(12)
O(2)-N(1)-C(1)-C(5)	176.17(10)
C(2)-N(1)-C(1)-C(5)	9.27(18)
C(1)-N(1)-C(2)-C(3)	-22.01(18)
O(2)-N(1)-C(2)-C(3)	170.71(11)
N(1)-C(2)-C(3)-C(4)	46.37(17)
C(2)-C(3)-C(4)-C(5)	-59.18(17)
O(1)-C(1)-C(5)-C(4)	160.80(13)
N(1)-C(1)-C(5)-C(4)	-21.57(18)
C(3)-C(4)-C(5)-C(1)	46.40(18)
O(4)-N(2)-C(6)-O(3)	-2.47(16)
C(7)-N(2)-C(6)-O(3)	-178.17(12)
O(4)-N(2)-C(6)-C(10)	177.28(9)
C(7)-N(2)-C(6)-C(10)	1.58(18)
C(6)-N(2)-C(7)-C(8')	-28.4(3)
O(4)-N(2)-C(7)-C(8')	155.8(2)
C(6)-N(2)-C(7)-C(8)	13.0(2)
O(4)-N(2)-C(7)-C(8)	-162.85(13)
N(2)-C(7)-C(8)-C(9)	-44.4(2)
C(7)-C(8)-C(9)-C(10)	61.8(3)
C(8)-C(9)-C(10)-C(6)	-48.1(3)
O(3)-C(6)-C(10)-C(9)	-163.59(17)
N(2)-C(6)-C(10)-C(9)	16.7(2)
O(3)-C(6)-C(10)-C(9')	169.6(3)
N(2)-C(6)-C(10)-C(9')	-10.1(3)
N(2)-C(7)-C(8')-C(9')	59.2(4)
C(7)-C(8')-C(9')-C(10)	-69.3(5)
C(6)-C(10)-C(9')-C(8')	46.0(5)

Table 7. Hydrogen bonds for $C_5H_9NO_2$ [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2O)...O(3)	0.88(2)	1.73(2)	2.6101(13)	176.3(18)
O(4)-H(4O)...O(1)#1	0.868(18)	1.789(18)	2.6383(14)	165.4(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z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C4
C1
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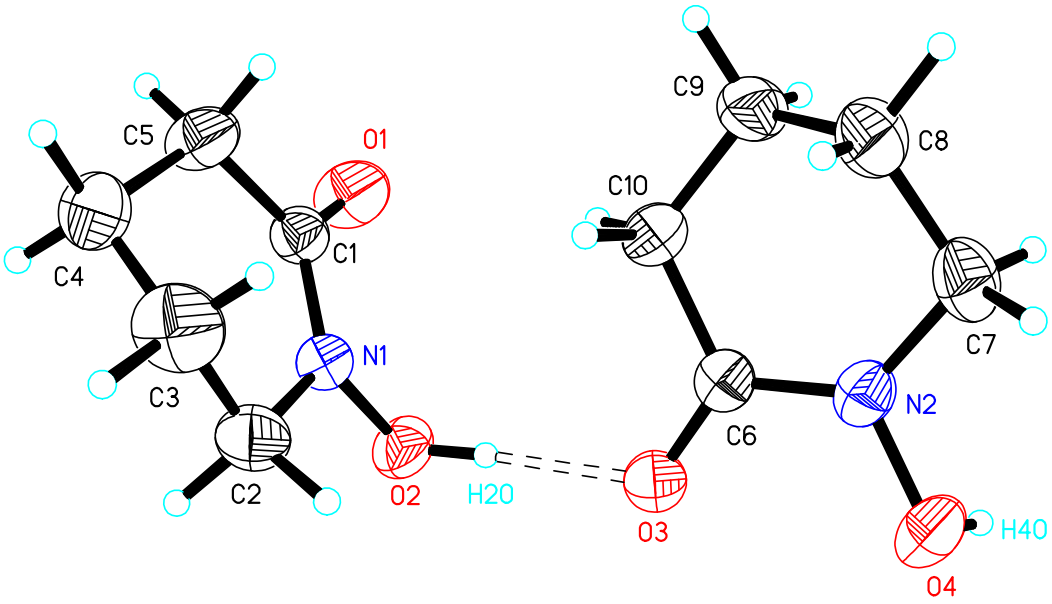
O4
H40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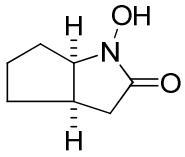
X-Ray Report for **4**



4

Crystals of $C_7H_{11}NO_2$ contain two crystallographically-independent molecules per asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level in thermal ellipsoid plots.

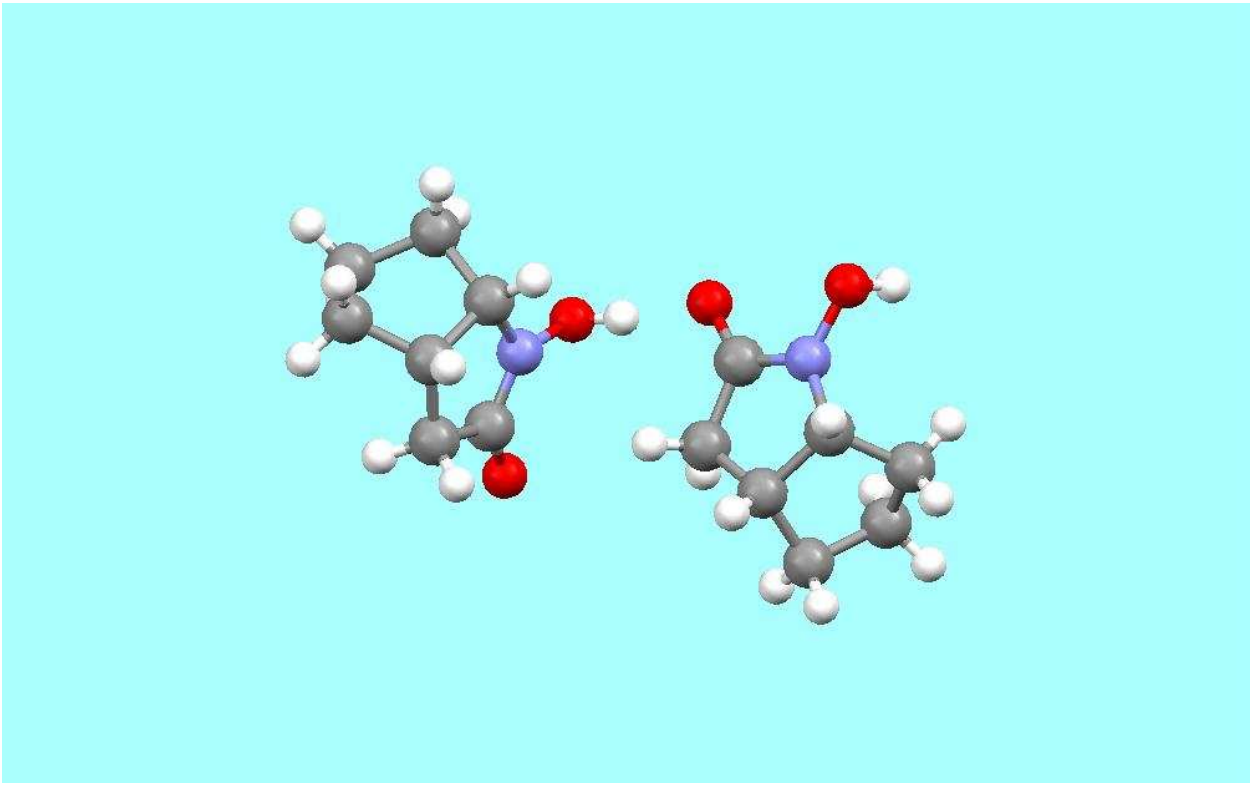


Table 1. Crystal data and structure refinement for $C_7H_{11}NO_2$

Identification code	a11m
Empirical formula	C7 H11 N O2
Formula weight	141.17
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c - C_{2h}^5 (No. 14)
Unit cell dimensions	a = 13.040(3) Å
	b = 10.086(3) Å, β = 92.336(3)°
	c = 10.802(3) Å
Volume	1419.5(6) $Å^3$
Z	8
Density (calculated)	1.321 g/cm^3
Absorption coefficient	0.097 mm^{-1}
F(000)	608
Crystal size	0.18 x 0.12 x 0.08 mm^3
Theta range for data collection	4.03 to 25.00°
Index ranges	$-15 \le h \le 15$, $0 \le k \le 11$, $0 \le l \le 12$
Reflections collected	3820
Independent reflections	3822 [R(int) = 0.0000]
Completeness to theta = 25.00°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / parameters	3822 / 190
Goodness-of-fit on F^2	1.194
Final R indices [I>2sigma(I)]	$R_1 = 0.0684$, $wR_2 = 0.1301$
R indices (all data)	$R_1 = 0.0845$, $wR_2 = 0.1365$
Largest diff. peak and hole	0.213 and -0.172 $e^-/Å^3$

$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR_2 = \{ \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \}^{1/2}$

Table 3. Bond lengths [Å] and angles [°] for $C_7H_{11}NO_2$ [a,b]

O(1A)-N(1A)	1.387(2)	O(1B)-N(1B)	1.383(2)
O(1A)-H(1A)	0.94(2)	O(1B)-H(1B)	0.90(3)
O(2A)-C(1A)	1.237(2)	O(2B)-C(1B)	1.230(3)
N(1A)-C(1A)	1.327(3)	N(1B)-C(1B)	1.321(3)
N(1A)-C(2A)	1.454(3)	N(1B)-C(2B)	1.456(3)
C(1A)-C(4A)	1.495(3)	C(1B)-C(4B)	1.496(3)
C(2A)-C(5A)	1.519(3)	C(2B)-C(5B)	1.520(3)
C(2A)-C(3A)	1.549(3)	C(2B)-C(3B)	1.553(3)
C(3A)-C(7A)	1.524(3)	C(3B)-C(7B)	1.520(3)
C(3A)-C(4A)	1.528(3)	C(3B)-C(4B)	1.529(3)
C(5A)-C(6A)	1.518(3)	C(5B)-C(6B)	1.518(4)
C(6A)-C(7A)	1.519(3)	C(6B)-C(7B)	1.506(4)
N(1A)-O(1A)-H(1A)	105.1(14)	N(1B)-O(1B)-H(1B)	104.9(18)
C(1A)-N(1A)-O(1A)	121.53(18)	C(1B)-N(1B)-O(1B)	121.56(17)
C(1A)-N(1A)-C(2A)	117.47(17)	C(1B)-N(1B)-C(2B)	117.72(18)
O(1A)-N(1A)-C(2A)	119.07(16)	O(1B)-N(1B)-C(2B)	120.34(18)
O(2A)-C(1A)-N(1A)	125.3(2)	O(2B)-C(1B)-N(1B)	126.4(2)
O(2A)-C(1A)-C(4A)	127.2(2)	O(2B)-C(1B)-C(4B)	126.2(2)
N(1A)-C(1A)-C(4A)	107.48(18)	N(1B)-C(1B)-C(4B)	107.37(19

N(1A)-C(2A)-C(5A)	111.66(18)	C(1A)-C(4A)-C(3A)	106.69(18)
N(1A)-C(2A)-C(3A)	102.36(17)	C(6A)-C(5A)-C(2A)	103.55(19)
C(5A)-C(2A)-C(3A)	106.47(18)	C(5A)-C(6A)-C(7A)	102.39(19)
C(7A)-C(3A)-C(4A)	114.47(19)	C(6A)-C(7A)-C(3A)	104.17(19)
N(1B)-C(2B)-C(5B)	112.04(19)	C(7B)-C(3B)-C(2B)	104.7(2)
N(1B)-C(2B)-C(3B)	102.35(18)	C(4B)-C(3B)-C(2B)	105.41(17)
C(5B)-C(2B)-C(3B)	105.7(2)	C(1B)-C(4B)-C(3B)	106.87(19)
C(7B)-C(3B)-C(4B)	113.6(2)	C(6B)-C(5B)-C(2B)	104.6(2)
C(7A)-C(3A)-C(2A)	104.70(18)	C(7B)-C(6B)-C(5B)	102.0(2)
C(4A)-C(3A)-C(2A)	105.73(17)	C(6B)-C(7B)-C(3B)	104.6(2)

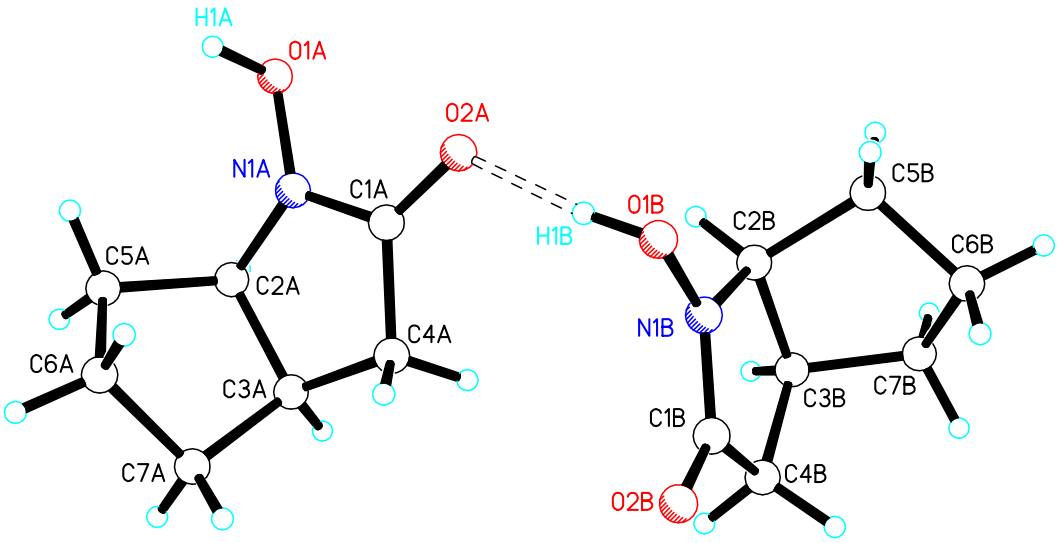
[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Figures 1 and 2.

Table 7. Inter-molecular Hydrogen bonds for $C_7H_{11}NO_2$ [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1A)-H(1A)...O(2B)#1	0.94(2)	1.71(3)	2.648(2)	178(2)
O(1B)-H(1B)...O(2A)	0.90(3)	1.69(3)	2.584(2)	173(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2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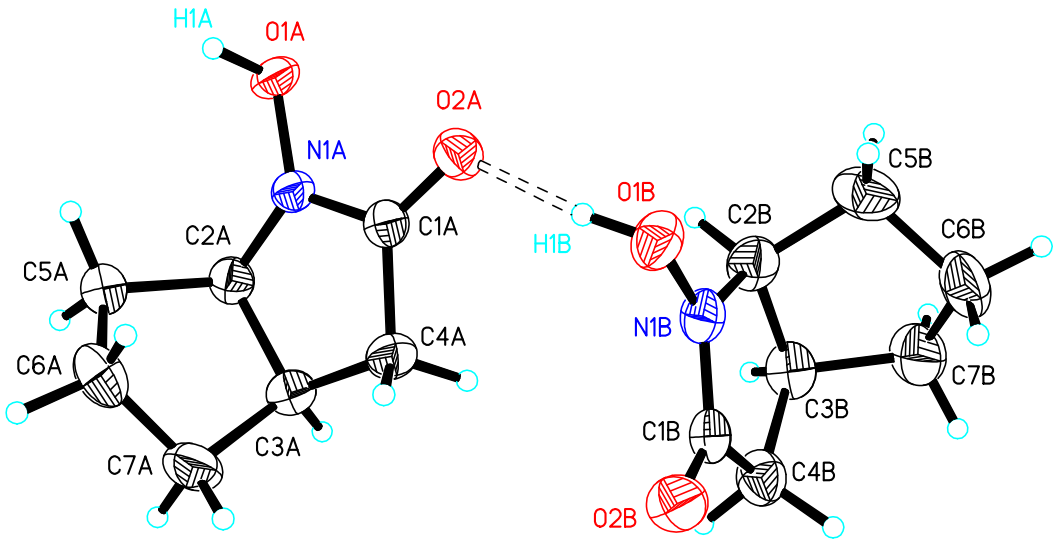
O1A
O2A
N1A
C1A
H1B
O1B
C2B
C5B
C5A
C2A
C6B
N1B
C4A
C6A
C3A
C3B
C7B
C1B
C7A
C4B
O2B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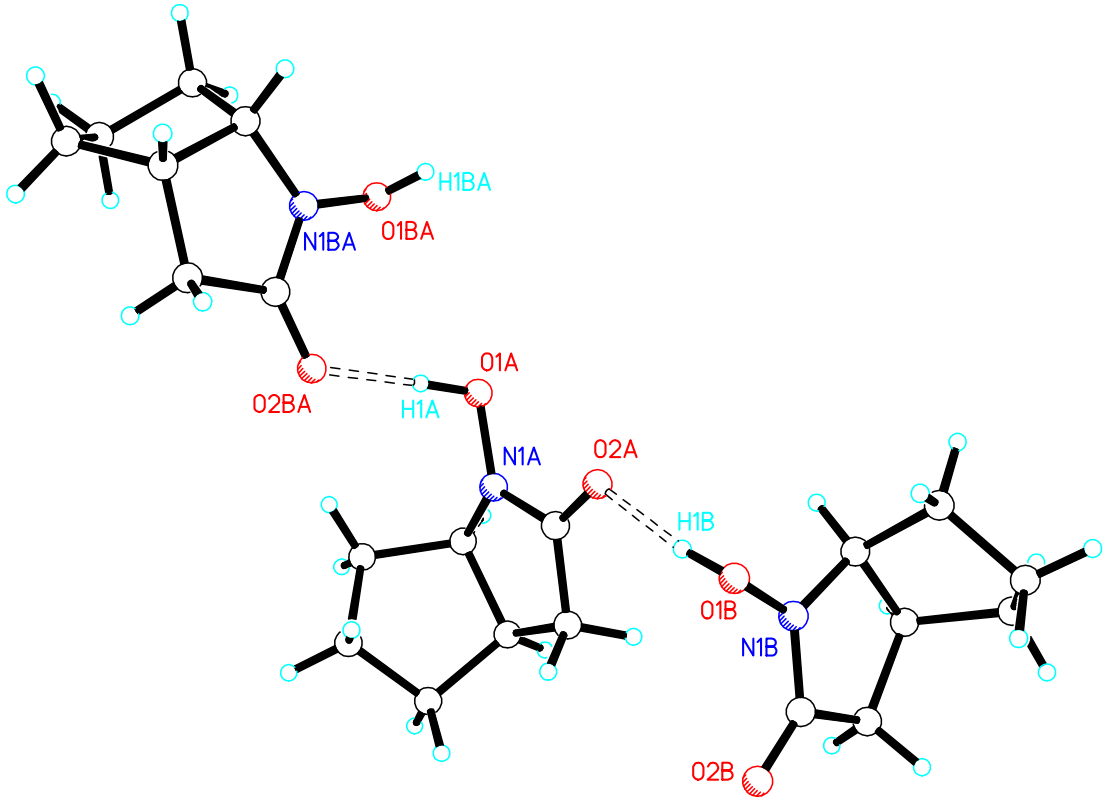
O1A
O2A
N1A
C1A
H1B
O1B
C2B
C5B
C5A
C2A
C6B
N1B
C4A
C6A
C3A
C3B
C7B
C1B
C7A
C4B
O2B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O1BA
N1BA
O1A
O2BA
H1A
N1A
O2A
H1B
O1B
N1B
O2B