

Chloral adduct of *N*-hydroxypiperidine

Wolfgang Kliegel,^a Ulf Riebe,^a
Brian O. Patrick,^b Steven J.
Rettig^b and James Trotter^{b*}

^aInstitut für Pharmazeutische Chemie, Technische Universität Braunschweig, Beethovenstrasse 55, 38106 Braunschweig, Germany, and

^bDepartment of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

Correspondence e-mail:
brian@xray5.chem.ubc.ca

Key indicators

Single-crystal X-ray study

$T = 294\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$

R factor = 0.043

wR factor = 0.046

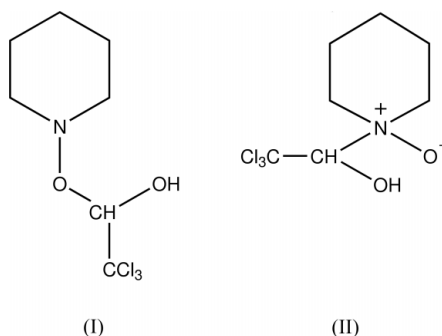
Data-to-parameter ratio = 11.5

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

The title compound, *N*-(2,2,2-trichloro-1-hydroxyethoxy)-piperidine, $\text{C}_7\text{H}_{12}\text{Cl}_3\text{NO}_2$, contains a six-membered piperidine ring with a chair conformation. The triclinic unit cell contains two independent pairs of molecules, with the molecules in each pair linked about centres of symmetry by $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds.

Comment

The title compound, (I), was synthesized according to a method described in the literature (Zinner *et al.*, 1965). On the basis of the results of boron chelate formation (Kliegel, 1969; Rettig *et al.*, 1974), the molecular structure reported for the adducts of carbonyl compounds and *N*-hydroxydialkylamines has generally to be questioned (Kliegel *et al.*, 1995). The present X-ray crystallographic analysis of (I) confirms that the α -hydroxyalkylation of *N*-hydroxypiperidine with chloral (trichloroacetaldehyde) leads to an *O*-alkyl derivative (*O*-semiacetal) and not to the isomeric *N*-oxide (II).



The crystal structure of (I) contains two independent molecules, which have virtually identical conformations and dimensions. The molecule contains a six-membered piperidine ring system, with a chair conformation (ring torsion angles in the range 53.4 to 63.0°). The substituent on the N atom is in an equatorial site, with the lone-pair electrons axial. Bond lengths and angles are all normal. The two independent molecules are linked into separate pairs about centres of symmetry (at $0, 1/2, 0$ and $0, 0, 1/2$) by $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds: $\text{O}\cdots\text{N} = 2.892(5), 2.815(5)\text{ \AA}$; $\text{H}\cdots\text{N} = 2.10(4), 2.04(5)\text{ \AA}$; $\text{O}-\text{H}\cdots\text{N} = 161(4), 164(5)^\circ$. There are some strong intermolecular interactions involving the Cl atoms, with $\text{Cl}\cdots\text{Cl}$ [$3.390(2)$ and $3.451(2)\text{ \AA}$] and $\text{Cl}\cdots\text{O}$ [$2.952(3)\text{ \AA}$] distances slightly shorter than normal van der Waals contacts (3.60 and 3.20 \AA , respectively); there are also some possible intermolecular $\text{C}-\text{H}\cdots\text{Cl}$ interactions: $\text{C}\cdots\text{Cl} = 3.67-3.75$, $\text{H}\cdots\text{Cl} = 2.72-2.84\text{ \AA}$ and $\text{C}-\text{H}\cdots\text{Cl} = 164-175^\circ$.

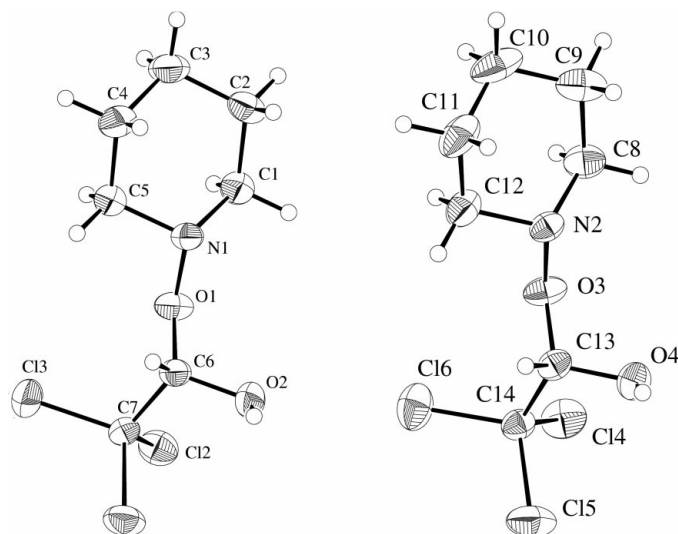


Figure 1
Views of the two independent molecules (33% probability ellipsoids).

Experimental

Compound (I) was prepared according to the literature method of Zinner *et al.* (1965); colourless crystals, m.p. 356–57 K (literature 358 K). IR (KBr): 3096 cm^{-1} (broad O–H); ^1H NMR (90 MHz, CDCl_3/TMS), δ (p.p.m.): 1.0–2.0 [*m*, $\text{C}(\text{CH}_2)_3\text{C}$], 2.4–3.6 [*m*, $\text{N}(\text{CH}_2)_2$], 5.30 (*d*, 6 Hz, O–CH–O), 7.00 (*s*, broad, exchangeable, OH). Crystals suitable for X-ray analysis were obtained by slow (48 h) crystallization from chloroform and cyclohexane using a liquid-diffusion method (Jones, 1981).

Crystal data

$\text{C}_7\text{H}_{12}\text{Cl}_3\text{NO}_2$
 $M_r = 248.54$
Triclinic, $P1$
 $a = 10.409$ (1) Å
 $b = 11.922$ (2) Å
 $c = 10.291$ (1) Å
 $\alpha = 109.78$ (1)°
 $\beta = 94.96$ (1)°
 $\gamma = 110.61$ (1)°
 $V = 1093.8$ (3) Å³

$Z = 4$
 $D_x = 1.509$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 39.6$ – 45.4 °
 $\mu = 7.37$ mm^{-1}
 $T = 294$ K
Block, colourless
 $0.40 \times 0.35 \times 0.30$ mm

Data collection

Rigaku AFC-6S diffractometer
 ω – 2θ scans
Absorption correction: ψ scan
(Molecular Structure Corporation, 1992)
 $T_{\min} = 0.076$, $T_{\max} = 0.110$
4696 measured reflections
4443 independent reflections
2810 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 77.5$ °
 $h = 0 \rightarrow 13$
 $k = -14 \rightarrow 14$
 $l = -12 \rightarrow 11$
3 standard reflections
every 200 reflections
intensity decay: none

Refinement

Refinement on F
 $R = 0.043$
 $wR = 0.046$
 $S = 1.95$
2810 reflections
244 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/\sigma^2(F_o)$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.24$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.21$ e \AA^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient:
 7.2 (4) $\times 10^{-6}$

Table 1

Selected geometric parameters (Å, °).

C11–C7	1.773 (3)	N1–C5	1.472 (4)
C12–C7	1.747 (4)	N2–C8	1.467 (4)
C13–C7	1.765 (3)	N2–C12	1.459 (4)
C14–C14	1.758 (4)	C1–C2	1.518 (6)
C15–C14	1.760 (3)	C2–C3	1.508 (5)
C16–C14	1.767 (4)	C3–C4	1.518 (6)
O1–N1	1.470 (3)	C4–C5	1.502 (6)
O1–C6	1.397 (4)	C6–C7	1.549 (6)
O2–C6	1.376 (4)	C8–C9	1.532 (6)
O3–N2	1.459 (4)	C9–C10	1.514 (6)
O3–C13	1.402 (6)	C10–C11	1.500 (7)
O4–C13	1.374 (4)	C11–C12	1.510 (6)
N1–C1	1.478 (4)	C13–C14	1.540 (6)
N1–O1–C6	110.5 (3)	C11–C7–C6	108.3 (3)
N2–O3–C13	110.4 (3)	C12–C7–C13	110.2 (2)
O1–N1–C1	103.2 (3)	C12–C7–C6	112.5 (3)
O1–N1–C5	104.9 (3)	C13–C7–C6	109.8 (2)
C1–N1–C5	109.9 (3)	N2–C8–C9	110.0 (4)
O3–N2–C8	103.1 (3)	C8–C9–C10	111.0 (4)
O3–N2–C12	105.4 (3)	C9–C10–C11	109.7 (4)
C8–N2–C12	110.4 (3)	C10–C11–C12	110.6 (4)
N1–C1–C2	110.2 (3)	N2–C12–C11	109.1 (3)
C1–C2–C3	111.9 (4)	O3–C13–O4	110.6 (3)
C2–C3–C4	109.0 (4)	O3–C13–C14	104.0 (3)
C3–C4–C5	111.1 (3)	O4–C13–C14	110.3 (2)
N1–C5–C4	110.3 (3)	C14–C14–C15	108.6 (2)
O1–C6–O2	110.3 (3)	C14–C14–C16	109.2 (3)
O1–C6–C7	103.7 (3)	C14–C14–C13	111.9 (3)
O2–C6–C7	110.6 (3)	C15–C14–C16	108.2 (3)
C11–C7–C12	108.8 (2)	C15–C14–C13	108.9 (3)
C11–C7–C13	107.1 (3)	C16–C14–C13	110.0 (2)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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