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A second polymorphic form of pentazocine hydrochloride at 105 K

Arvid Mostad

Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

Correspondence e-mail: arvidm@kjemi.uio.no

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Key indicators

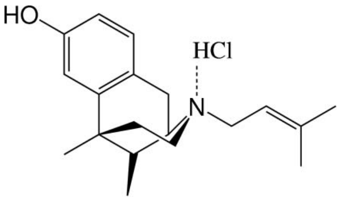
Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.102
Data-to-parameter ratio = 14.7

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

The crystal structure of pentazocine hydrochloride [systematic name: 2-hydroxy-5,9-dimethyl-2-(3-methylbuten-2-yl)-6,7-benzomorphanium chloride], $C_{19}H_{28}NO^+\cdot Cl^-$, has been determined at 105 K and found to be a second polymorphic form with space group *C*2/*c*. The space group and the unit-cell parameters are different from a reported crystal structure at 293 K [Majeste, Poindexter, Jones & Klein (1994). *Acta Cryst.* C**50**, 1633–1636]. There are only small differences in the molecular conformation, but the association between the protonated pentazocine molecules and the chloride ion is different.

Comment

The crystal structure of pentazocine hydrochloride, (I), has been reported to exist at room temperature in space group $P2_1/c$ with two independent molecules in the asymmetric unit (Majeste *et al.*, 1994). However, an examination of crystals of pentazocine hydrochloride at 105 K has shown that the compound also exists in space group *C*2/*c* with a different mode of packing around the chloride ions. The molecular structure and atom numbering are given in Fig. 1.



(I)

Each chloride ion is hydrogen bonded to atoms N1 and O1 of two different cations, as shown in Fig. 2 and described in Table 2. The angle N1···Cl1···O1($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$) is 107.60° in the present study, in contrast to 168.80 (8)° reported for a similar linkage in the room-temperature structure. In addition to the hydrogen bonding to N1 and O1, the distance Cl1···H15*B*($-x$, $1-y$, $1-z$) is very short, only 2.69 (2) Å. The geometry of this contact, as well that of another close contact, between C14—H14 and O1, are given in Table 2.

The packing is depicted in Fig. 3, where the shortest contacts are also indicated. In spite of the difference in the space group and packing, there are only minor, though significant, differences in the molecular structure and conformation. Even the rather large displacement parameters seen for atom C16 in the high-temperature structure are also seen for the equivalent atom (C18) in the present structure.

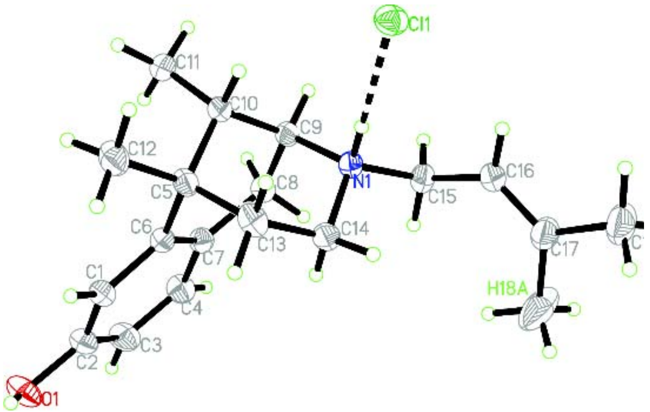


Figure 1
A view of the asymmetric unit of (I), showing the atom numbering and displacement ellipsoids at the 50% probability level. The dashed line indicates a hydrogen bond.

The torsion angle C15—C16—C17—C18 is −2.2 (3)°, bringing C18 and C15 into close contact; internal strain is also indicated by the angles C15—C16—C17 of 127.2 (1)° and C16—C17—C18 of 125.0 (1)°. This planar configuration, a consequence of the double bond between atoms C16 and C17, is also influenced by rather short contacts between neighboring chloride ions and atoms H16, H18*A* and H15*A*, the distances being 2.91 (2), 3.03 (2) and 3.03 (2) Å, respectively.

Experimental

The title compound was recrystallized from ethanol. The compound was purchased from Winthrop Laboratories, Newcastle, in 1978 in connection with our work on some similar compounds. In 2004, prismatic needle crystals were found in a test tube that originally contained the compound in an ethanol solution.

Crystal data

$C_{19}H_{28}NO^{+}\cdot Cl^{-}$
$M_r = 321.87$
Monoclinic, $C2/c$
$a = 24.541\ (5)$ Å
$b = 11.537\ (2)$ Å
$c = 14.897\ (3)$ Å
$\beta = 119.05\ (3)^\circ$
$V = 3687\ (1)$ Å^3
$Z = 8$
$D_x = 1.160$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23580 reflections
$\theta = 2.3$–28.4°
$\mu = 0.21$ mm^{-1}
$T = 105\ (2)$ K
Needle, colorless
0.5 × 0.2 × 0.2 mm

Data collection

Bruker SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.896$, $T_{\max} = 0.957$
28837 measured reflections
4582 independent reflections
4113 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 28.3^\circ$
$h = -32 \rightarrow 32$
$k = -15 \rightarrow 15$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.102$
$S = 1.04$
4582 reflections
311 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 2.1933P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.369 (1)	C8—C9	1.530 (2)
N1—C14	1.497 (2)	C9—C10	1.532 (1)
N1—C9	1.515 (1)	C10—C11	1.532 (2)
N1—C15	1.518 (1)	C13—C14	1.516 (2)
C5—C6	1.528 (1)	C15—C16	1.502 (2)
C5—C12	1.536 (2)	C16—C17	1.326 (2)
C5—C13	1.549 (2)	C17—C18	1.498 (2)
C5—C10	1.552 (2)	C17—C19	1.509 (2)
C7—C8	1.519 (2)		
C14—N1—C9	111.4 (1)	C7—C8—C9	115.3 (1)
C14—N1—C15	111.0 (1)	N1—C9—C8	112.7 (1)
C9—N1—C15	114.1 (1)	N1—C9—C10	108.0 (1)
O1—C2—C3	117.7 (1)	C8—C9—C10	111.6 (1)
O1—C2—C1	122.5 (1)	C10—C9—H9	110 (1)
C6—C5—C12	112.8 (1)	C11—C10—C9	109.9 (1)
C6—C5—C13	109.0 (1)	C11—C10—C5	114.2 (1)
C12—C5—C13	107.3 (1)	C9—C10—C5	109.0 (1)
C6—C5—C10	109.8 (1)	C14—C13—C5	112.9 (1)
C12—C5—C10	110.0 (1)	N1—C14—C13	110.1 (1)
C13—C5—C10	107.7 (1)	C16—C15—N1	109.7 (1)
C7—C6—C5	120.0 (1)	C17—C16—C15	127.2 (1)
C1—C6—C5	120.7 (1)	C16—C17—C18	125.0 (1)
C4—C7—C8	118.4 (1)	C16—C17—C19	120.6 (1)
C6—C7—C8	122.7 (1)	C18—C17—C19	114.4 (1)
C2—C1—C6—C5	179.9 (1)	N1—C9—C10—C5	−63.4 (1)
C12—C5—C6—C7	153.0 (1)	C8—C9—C10—C5	61.0 (1)
C13—C5—C6—C7	−87.9 (10)	C6—C5—C10—C11	64.3 (10)
C10—C5—C6—C7	29.9 (1)	C12—C5—C10—C11	−60.4 (1)
C12—C5—C6—C1	−28.9 (1)	C13—C5—C10—C11	−177.1 (1)
C13—C5—C6—C1	90.2 (1)	C6—C5—C10—C9	−59.1 (1)
C10—C5—C6—C1	−152.0 (1)	C12—C5—C10—C9	176.2 (1)
C3—C4—C7—C8	−179.1 (1)	C13—C5—C10—C9	59.5 (1)
C1—C6—C7—C8	−179.3 (1)	C6—C5—C13—C14	63.6 (1)
C5—C6—C7—C8	−1.2 (2)	C12—C5—C13—C14	−173.9 (1)
C4—C7—C8—C9	−178.7 (1)	C10—C5—C13—C14	−55.6 (1)
C6—C7—C8—C9	1.8 (2)	C9—N1—C14—C13	−57.5 (1)
C14—N1—C9—C8	−61.2 (1)	C15—N1—C14—C13	174.1 (1)
C15—N1—C9—C8	65.5 (1)	C5—C13—C14—N1	54.5 (1)
C14—N1—C9—C10	62.5 (1)	C14—N1—C15—C16	−76.5 (1)
C15—N1—C9—C10	−170.7 (1)	C9—N1—C15—C16	156.5 (1)
C7—C8—C9—N1	89.8 (1)	N1—C15—C16—C17	122.0 (1)
C7—C8—C9—C10	−31.9 (1)	C15—C16—C17—C18	−2.2 (3)
N1—C9—C10—C11	170.6 (1)	C15—C16—C17—C19	177.8 (10)
C8—C9—C10—C11	−65.0 (1)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15B···Cl1$^{\rm i}$	0.97 (2)	2.69 (2)	3.644 (2)	171 (1)
N1—H1N···Cl1$^{\rm ii}$	0.90 (2)	2.23 (2)	3.126 (1)	175 (1)
O1—H20···Cl1$^{\rm iii}$	0.87 (2)	2.24 (2)	3.089 (1)	168 (2)
C14—H14B···O1$^{\rm iv}$	0.95 (2)	2.49 (1)	3.153 (2)	127 (1)

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

All H atoms were located in difference maps and, except for the H atoms bonded to C18, were refined by isotropic approximation. The relatively large displacement of C18 approximately perpendicular to the C15/C16/C17/C18 plane may be induced by the crowded environment of the C18 methyl group. The large anisotropy is believed to indicate large restrictions in vibrational freedom, or possibly a slight disorder in the position of atom C18. The values of the displacement parameters for C18 are, however, not considered to be large enough

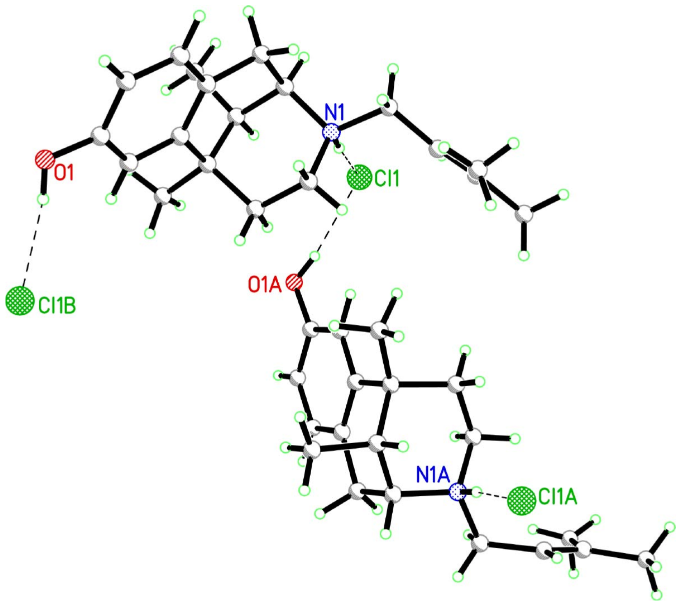


Figure 2
The bonding between protonated pentazocine molecules and the chloride ions. Ions A are at the symmetry position ($\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$). Dashed lines indicate hydrogen bonds.

to split atom C18. For this reason, the H atoms bonded to C18 were refined with riding constraints. Except for the distances involving H1N and H20, described in Table 2, the C—H distances are in the range 0.93 (1)–1.03 (1) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

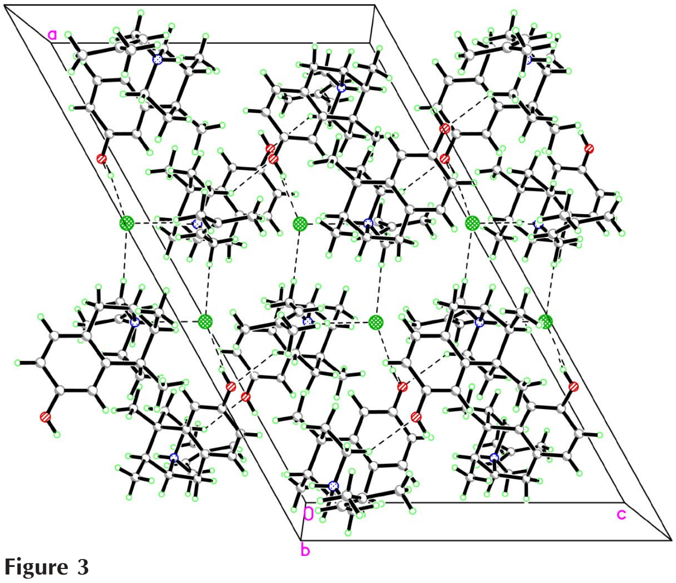


Figure 3
The packing of the ions in space group *C*2/*c*. Dashed lines indicate hydrogen bonds.

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