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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.044

wR factor = 0.105

Data-to-parameter ratio = 16.6

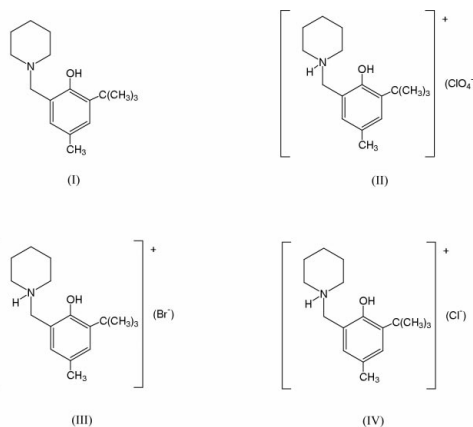
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

2-*tert*-Butyl-4-methyl-6-(1-piperidinio-methyl)phenol chloride

In the crystal structure of the title compound, $\text{C}_{17}\text{H}_{28}\text{NO}^+\cdot\text{Cl}^-$, the *N*-protonated piperidine ring adopts the normal chair conformation. Each chloride anion acts as an acceptor in $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds, resulting in an $R_2^1(8)$ ring pattern. Intermolecular $\text{C}-\text{H}\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions further extend these patterns to form a two-dimensional supramolecular network.

Comment

The design and synthesis of new piperidine derivatives have attracted much interest owing to their application in anti-cancer drugs (Varvaresou *et al.*, 1996), high active serotonergic agents (Radl *et al.*, 1999) and other areas of clinical medicine (Orjales *et al.*, 1995). Recently, we reported the synthesis and crystal structures of 2-*tert*-butyl-4-methyl-6-(piperidyl-*N*-methyl)phenol, (I) (Deng *et al.*, 2001), and its *N*-protonated perchlorate and bromide, (II) and (III) (Zhao & Du, 2003; Du & Zhao, 2003). We report here the synthesis and crystal structure of the *N*-protonated chloride of (I), namely 2-*tert*-butyl-4-methyl-6-(1-piperidiniomethyl)phenol chloride, (IV).



The crystal structure of (IV) consists of a $\text{C}_{17}\text{H}_{28}\text{NO}^+$ cation and a Cl^- counter-anion, as shown in Fig. 1. As in its analogues, (I), (II) and (III), the piperidine ring adopts a normal chair conformation. The chair geometry is slightly distorted from ideal, the ring torsion angles lying in the range $55.7(3)$ – $58.3(3)^\circ$. In (I), (II) and (III), these angles are in the ranges $52.5(4)$ – $59.8(3)$, $55.3(4)$ – $56.8(5)$ and $56.3(10)$ – $58.5(13)^\circ$, respectively.

The C–C and C–N bond lengths in the piperidine ring (mean values: 1.508 and 1.493 Å; Table 1) can be compared with the values in (I) (1.515 and 1.461 Å), (II) (1.513 and 1.500 Å) and (III) (1.524 and 1.513 Å). The slightly longer C–N bond distances in (II), (III) and (IV), compared with those in (I), may be due to the protonation of the piperidine ring.

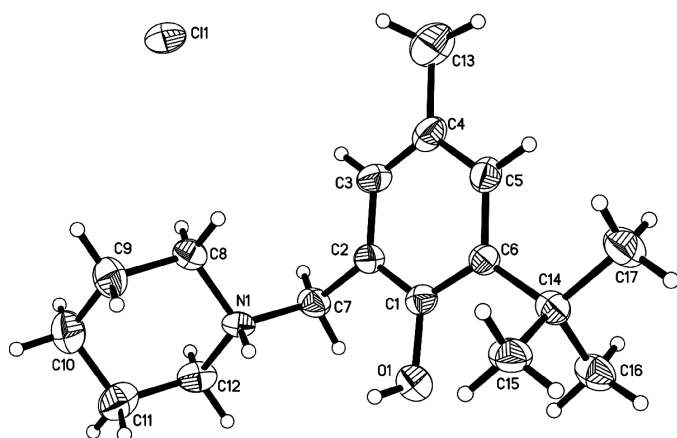


Figure 1
A view of (IV), with displacement ellipsoids drawn at the 30% probability level. H atoms are represented by spheres of arbitrary radius.

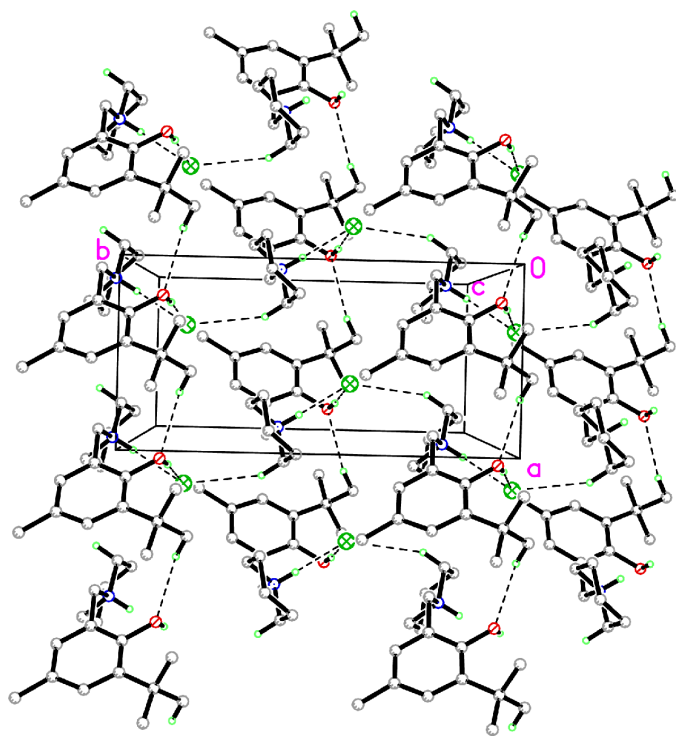


Figure 2
A view of the hydrogen-bonding pattern of (IV). Hydrogen bonds are indicated by dashed lines.

The orientations of the piperidine ring and the benzene ring in (III) and (IV) are same; this is reflected by the torsion angles N1–C7–C2–C1 [$-84.1(10)^\circ$ for (III) and $84.0(3)^\circ$ for (IV)] and N1–C7–C2–C3 [$100.2(10)^\circ$ for (III) and $-98.4(3)^\circ$ for (IV)]. The orientations of these rings in (II) are different and the corresponding torsion angles are $103.6(4)^\circ$ and $-77.9(4)^\circ$.

Analysis of the crystal packing of the title compound reveals the existence of an O–H...Clⁱ [symmetry code: (i) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$] hydrogen bond between the phenolic O atom and the chloride anion. An N–H...Clⁱ hydrogen bond is also present, involving the protonated piperidine N atom and

the Cl⁻ anion. According to the formalism of graph-set patterns (Etter, 1990), the resulting motif (Fig. 2) is characterized as an $R_2^2(8)$ ring pattern.

In addition, an intermolecular C–H...Clⁱⁱ [symmetry code: (ii) $x-1, y, z$] interaction between the C12 atom in the protonated piperidine ring and the chloride ion, and a C–H...Oⁱⁱⁱ [symmetry code: (iii) $x+1, y, z$] interaction between the C15 atom of the *tert*-butyl group and the phenol oxygen acceptor, further extend these patterns to form a two-dimensional layered supramolecular network along the [110] direction, as shown in Fig. 2. The relevant geometrical details are listed in Table 2; these values are in the normal range for weak hydrogen-bonding interactions (Desiraju & Steiner, 1999). Examination of the structure with PLATON (Spek, 2003) indicates that there are no solvent-accessible voids nor π – π stacking interactions in the crystal structure of (IV).

Experimental

2-*tert*-Butyl-4-methyl-6-(piperidyl-*N*-methyl)phenol was prepared as in our previous work (Deng *et al.*, 2001). Colourless block single crystals of the title compound, (IV), suitable for X-ray diffraction were obtained, in 90% yield, by slow evaporation of a methanol solution of 2-*tert*-butyl-4-methyl-6-(piperidyl-*N*-methyl)phenol in the presence of HCl. Analysis calculated for (IV): C 68.55, H 9.47, N 4.70%; found: C 68.69, H 9.72, N 4.68%. FT-IR data (KBr pellet, cm^{-1}): 3423 (*b*), 3074 (*m*), 3005 (*w*), 2953 (*m*), 2871 (*m*), 2797 (*w*), 2775 (*w*), 2675 (*m*), 2652 (*m*), 2554 (*m*), 2392 (*w*), 1761 (*w*), 1607 (*w*), 1477 (*vs*), 1453 (*vs*), 1443 (*vs*), 1432 (*vs*), 1397 (*s*), 1359 (*m*), 1343 (*w*), 1319 (*w*), 1286 (*m*), 1262 (*s*), 1233 (*vs*), 1222 (*vs*), 1157 (*m*), 1142 (*m*), 1078 (*w*), 1038 (*w*), 979 (*w*), 960 (*m*), 941 (*s*), 923 (*w*), 894 (*m*), 865 (*s*), 803 (*w*), 788 (*w*), 771 (*w*), 757 (*m*), 664 (*w*), 625 (*m*), 596 (*w*), 580 (*m*), 539 (*m*), 527 (*w*).

Crystal data

C₁₇H₂₈NO⁺·Cl⁻
 $M_r = 297.85$
 Orthorhombic, $P2_12_12_1$
 $a = 5.882(2) \text{ \AA}$
 $b = 12.187(5) \text{ \AA}$
 $c = 24.553(10) \text{ \AA}$
 $V = 1760.1(12) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.124 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 827 reflections
 $\theta = 3.3\text{--}22.8^\circ$
 $\mu = 0.21 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, colourless
 $0.34 \times 0.32 \times 0.20 \text{ mm}$

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.841, T_{\max} = 1.000$
 7868 measured reflections

3092 independent reflections
 2288 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\max} = 25.0^\circ$
 $h = -5 \rightarrow 7$
 $k = -14 \rightarrow 13$
 $l = -29 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.105$
 $S = 1.02$
 3092 reflections
 186 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983);
 1275 Friedel pairs
 Flack parameter = $-0.11(8)$

Table 1

Selected geometric parameters (Å, °).

N1—C8	1.493 (3)	C8—C9	1.502 (4)
N1—C12	1.493 (3)	C9—C10	1.506 (5)
N1—C7	1.507 (3)	C10—C11	1.502 (5)
O1—C1	1.387 (3)	C11—C12	1.523 (4)
C8—N1—C12	110.98 (19)	O1—C1—C2	117.6 (2)
C8—N1—C7	111.88 (19)	O1—C1—C6	120.6 (2)
C12—N1—C7	110.1 (2)	C2—C1—C6	121.8 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...C11 ⁱ	0.91	2.23	3.137 (3)	173
O1—H1A...CH ⁱ	0.82	2.23	3.047 (3)	174
C12—H12B...C11 ⁱⁱ	0.97	2.91	3.799 (4)	153
C15—H15C...O1 ⁱⁱⁱ	0.96	2.56	3.487 (3)	162

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

Although most H atoms were visible in difference maps, all H atoms were placed in geometrically calculated positions (0.97 Å for methylene C—H, 0.93 Å for aromatic C—H, 0.96 Å for methyl C—H, 0.91 Å for N—H and 0.82 Å for O—H) and included in the final refinement in the riding-model approximation, with displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$ for N—H, aromatic C—H and methylene C—H, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{carrier atom})$ for O—H and methyl C—H. A rotating-group model was used for the hydroxyl and methyl groups.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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