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N-[(*S*)-1-(5-Chloro-2-hydroxyphenyl)ethyl]-*N*-[(*R*)-2-hydroxy-1-phenylethyl]aminium chloride ethyl acetate solvate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
R factor = 0.067
wR factor = 0.178
Data-to-parameter ratio = 13.2

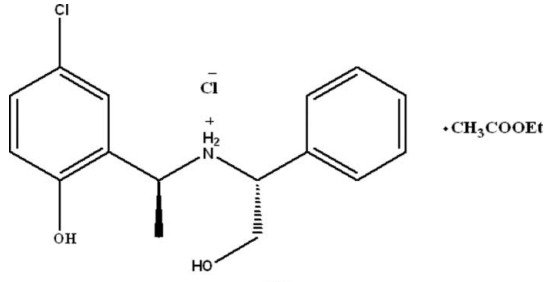
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{16}H_{19}ClNO_2^+\cdot Cl^-\cdot C_4H_8O_2$, was synthesised and its molecular structure determined. The absolute configuration of a new stereogenic centre is determined to be *S*. $N^+—H\cdots Cl^-$ and $O—H\cdots Cl^-$ interactions connect structural components, generating a hydrogen-bonded spiral along the twofold screw axis.

Comment

The development of new chiral aminoalkylphenols has been given considerable attention owing to their application in asymmetric synthesis, which is one of the most active areas in synthetic chemistry. Most of these aminoalkylphenols are derived from easily available natural products (Cardellicchio *et al.*, 1998; Duthaler, 1994; Kelin *et al.*, 2005; Puigjaner *et al.*, 1999; Pu & Yu, 2001; Soai & Niwa, 1992; Steiner *et al.*, 2002; Wang *et al.*, 2004; Xu & Pu, 2004; Zhang *et al.*, 2003).

Chiral amino acids can be converted into the corresponding amino alcohols by reduction with sodium borohydride (McKennon *et al.*, 1993). In our previous work, *R*-(−)-phenylglycinol was prepared by the same economical method. The precursor of known absolute configuration can be used as the internal standard for determination of the absolute configuration of a new chiral centre. The aminoalkylphenol was prepared by conventional condensation of 2-hydroxy-5-chloroacetophenone with *R*-(−)-phenylglycinol, followed by reduction with $NaBH_4$. Single crystals of the title compound, (I), were obtained from an *iso*-propanol/ethyl acetate solvent mixture.



(I)

The absolute configuration of (I) is shown in Fig. 1. In the synthesis of (I) a precursor of the *R* configuration was used, thus the new chiral centre C7 of (I) is determined to be of the *S* configuration. Selected bond lengths and angles of (I) are reported in Table 1. The dihedral angle between the planes of aromatic rings C1–C6 and C11–C16 is 38.59 (17)°. The crystal packing reveals ethyl acetate as a solvent molecule with significant but unresolved disorder (Fig. 1). The intermolecular $N^+—H\cdots Cl^-$ and $O—H\cdots Cl^-$ hydrogen bonds

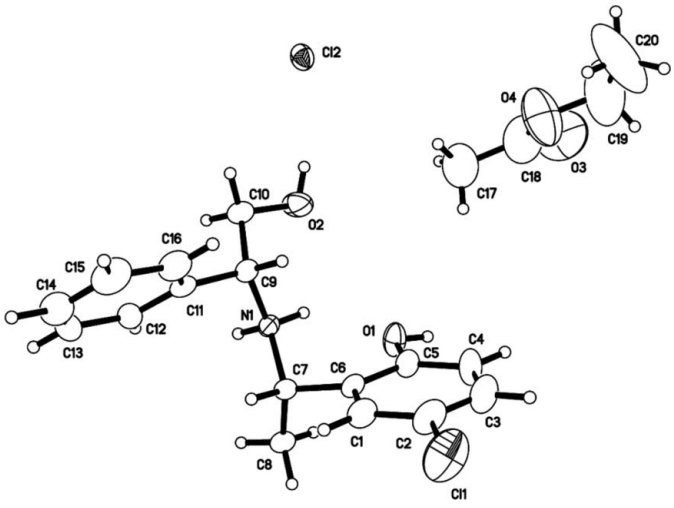


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level.

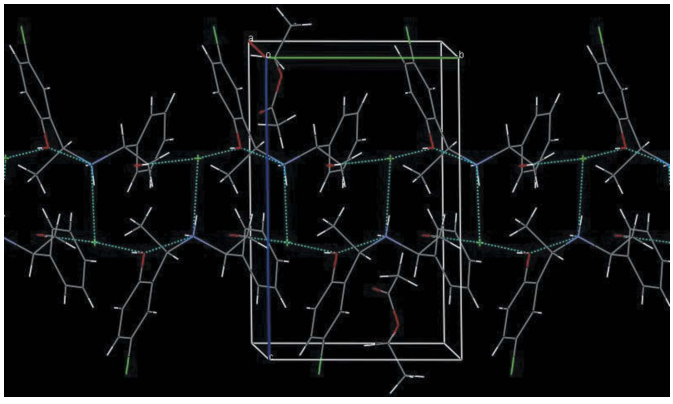


Figure 2
A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

together with an intramolecular $N^+—H\cdots O$ hydrogen bond create a hydrophilic layer. Hydrogen-bond parameters are listed in Table 2 and their pattern is shown in Fig. 2.

Experimental

R-(−)-Phenylglycinol was prepared by the reduction reaction of *R*-(−)-phenylglycine with $NaBH_4$ in tetraydrofuran (THF) {80.2% yield, $[\alpha]_D^{24}$= −25.5 (c_6, MeOH)} (Abiko & Masamune, 1992; Demir *et al.*, 1999; McKennon *et al.*, 1993). *R*-(−)-Phenylglycinol (2 mmol) and 2-hydroxy-5-chloroacetophenone (2 mmol) [*R*-(−)-phenylglycine, $NaBH_4$ and 2-hydroxy-5-chloroacetophenone were purchased from J & K Chemical Ltd]. Chemicals were dissolved in methanol (15 ml) and reacted at room temperature for 12 h. After the solvent was removed, THF/ethanol (15 ml, 1:1 *v*/*v*) and $NaBH_4$ (8 mmol) were added at 273 K. The reaction was quenched with 5 *M* HCl and neutralized by NaOH solution. The aqueous solution was extracted by $CHCl_3$, and the organic layer was dried with anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. Further purification was carried out by thin-layer sillica-gel chromatography (chloroform/methanol 30: 1). The chiral compound (I) was prepared in 80% yield, $[\alpha]_D^{16}$ = −76.5 ($c_{0.5}$, $CHCl_3$) (Yang *et al.*, 2005). Compound (I) (0.1 mmol) was dissolved in methanol (10 ml). Concentrated HCl (0.1 ml) was added at room temperature and a white solid was precipitated. The HCl salt was crystallized from an isopropanol/ethyl acetate mixture (1:20) (70% yield).

Crystal data

$C_{16}H_{19}ClNO_2^+\cdot Cl^-\cdot C_4H_8O_2$
M_r = 416.33
Monoclinic, $P2_1$
a = 11.912 (3) Å
b = 7.7221 (18) Å
c = 12.312 (3) Å
β = 103.993 (3)°
V = 1098.9 (4) Å^3
Z = 2
D_x = 1.258 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 298 (2) K
Block, colourless
0.35 × 0.21 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.897, T_{max} = 0.945
4637 measured reflections
3294 independent reflections
3077 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.178
S = 1.08
3294 reflections
249 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1181P)^2 + 0.0672P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 1195 Friedel pairs
Flack parameter: −0.03 (11)

Table 1
Selected geometric parameters (Å, °).

C2—Cl1	1.742 (5)	C9—C11	1.494 (6)
C5—O1	1.373 (5)	C9—N1	1.498 (5)
C6—C7	1.509 (5)	C9—C10	1.518 (6)
C7—N1	1.513 (5)		
O1—C5—C6	116.4 (4)	C11—C9—C10	112.9 (3)
C6—C7—N1	110.9 (3)	N1—C9—C10	106.8 (3)
N1—C7—C8	108.1 (3)	O2—C10—C9	109.1 (4)
C11—C9—N1	112.6 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$B\cdots$Cl2^{i}	0.90	2.28	3.154 (3)	163
O1—H1$\cdots$Cl2^{ii}	0.82	2.19	2.995 (3)	169
O2—H2$\cdots$Cl2	0.82	2.35	3.156 (4)	169
N1—H1$A\cdots$O1	0.90	2.00	2.718 (4)	135

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

All H atoms were positioned geometrically and treated as riding, with C—H = 0.93–0.98 Å, N—H = 0.90 Å and O—H = 0.82 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(C_{methyl},O).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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