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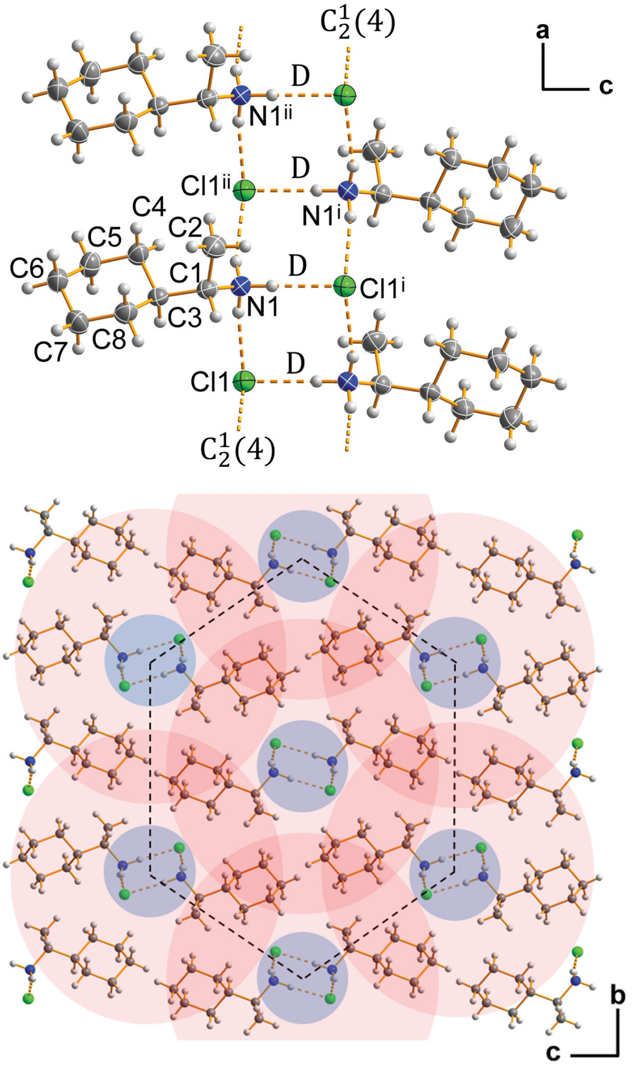
Crystal structure of (*S*)-(+)-1-cyclohexylethylaminium chloride, $C_8H_{18}NCl$



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Abstract

$C_8H_{18}NCl$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 5.5244(3)$ Å, $b = 11.0915(6)$ Å, $c = 16.0339(12)$ Å, $V = 982.46(11)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0295$, $wR_{ref}(F^2) = 0.0785$, $T = 233(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	0.90 × 0.30 × 0.22 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.33 mm^{-1}
Diffractometer, scan mode:	STOE IPDS 2T, ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17396, 2248, 0.130
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2242
$N(param)_{refined}$:	104
Programs:	SHELX [1, 2], Diamond [3]

Source of material

For the synthesis of (*S*)-(+)-1-cyclohexylethylaminium chloride 0.057 g (0.45 mmol) (*S*)-(+)-1-cyclohexylethylamine (Sigma-Aldrich) were mixed with 2 mL concentrated hydrochloric acid and 1 mL methanol. Colourless crystals (m.p. 521 K) suitable for X-ray crystal structure determination grew in the course of evaporating this solution to dryness under isothermal conditions (T = 293 K). Note that the compound crystallizes acicular with a strong tendency of the needles to break into thinner segments. Raman spectra were measured with a Bruker MultiRAM spectrometer equipped with a Nd:YAG laser (1064 nm) and an InGaAs detector. **Raman** 4000-70 cm^{-1}: ν(C—H): 3050 cm^{-1} (w); ν(N—H): 2972 cm^{-1} (m); ν(C—H): 2928 cm^{-1} (vs), 2860 cm^{-1} (s); δ_{as}(C—H): 1444 cm^{-1} (m). IR spectroscopic data were obtained with a Perkin-Elmer Spektrum Two FT-IR spectrometer equipped with a $LiTaO_3$ detector and universal ATR equipment. **IR** 4000-350 cm^{-1}: ν(N—H): 2969 cm^{-1} (m); ν(C—H): 2924 cm^{-1} (vs), 2883 cm^{-1} (s), 2854 cm^{-1} (s),

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	$U_{iso}*/U_{eq}$
Cl1	0.09050(8)	0.13794(4)	0.90935(3)	0.04724(14)
N1	0.5898(3)	0.27635(16)	0.90315(9)	0.0444(3)
H1	0.591(6)	0.306(3)	0.9595(19)	0.083(9)*
H2	0.718(5)	0.233(2)	0.8945(15)	0.051(6)*
H3	0.454(5)	0.234(2)	0.8988(16)	0.060(7)*
C1	0.5740(3)	0.37912(16)	0.84298(10)	0.0419(4)
H11	0.430457	0.427885	0.858132	0.050*
C2	0.7976(4)	0.4579(2)	0.85491(14)	0.0553(5)
H21	0.942117	0.409722	0.846500	0.083*
H22	0.798134	0.490713	0.910996	0.083*
H23	0.794914	0.523408	0.814835	0.083*
C3	0.5348(3)	0.33088(15)	0.75430(11)	0.0386(4)
H31	0.403387	0.270368	0.757415	0.046*
C4	0.7574(4)	0.26687(19)	0.71782(11)	0.0462(4)
H41	0.892637	0.323819	0.714409	0.055*
H42	0.805469	0.200627	0.754716	0.055*
C5	0.7024(4)	0.21738(19)	0.63133(12)	0.0511(5)
H51	0.848055	0.179046	0.608637	0.061*
H52	0.575879	0.155761	0.635539	0.061*
C6	0.6196(4)	0.3160(2)	0.57266(11)	0.0521(4)
H61	0.577808	0.280803	0.518493	0.063*
H62	0.751747	0.373628	0.564026	0.063*
C7	0.3998(4)	0.3819(2)	0.60811(13)	0.0585(5)
H71	0.357207	0.449187	0.571326	0.070*
H72	0.261602	0.326532	0.609972	0.070*
C8	0.4496(4)	0.42975(18)	0.69545(12)	0.0487(4)
H81	0.573596	0.492782	0.692381	0.058*
H82	0.301558	0.466201	0.717775	0.058*

δ(N—H): 1606 cm^{-1} (m), 1518 cm^{-1} (m), δ(C—H): 1455 cm^{-1} (w), 1395 cm^{-1} (w). The band assignments are based on [4]. A CHN analysis was performed with a Elementar Analysensysteme vario Micro CUBE. **EA** $C_8H_{18}NCl$ (163.688 g/mol): C 58.42, H 10.98, N 8.51; calc. C 58.70, H 11.08, N 8.56.

Experimental details

Positions of the H atoms bound to N1 and the majority of the hydrogen atoms bound to carbon atoms were identified by difference-Fourier synthesis. Coordinates and isotropic displacement parameters of the N-bonded H atoms were refined. For the C-bonded hydrogen atoms in the refinement a riding model was applied using idealized C—H bond lengths (0.97–0.99 Å) and H—C—H and C—C—H angles. In addition, the H atoms of the CH_3-group were allowed to rotate around the adjacent C—C bond. The $U_{iso}(C)$ values were set to $1.5U_{eq}(C_{methyl})$ and $1.2U_{eq}(C_{methylene}$ and $C_{methine})$. Absolute structure parameters were refined to 0.01(2) (Flack [5]) and 0.002(17) (Hooft [6]).

Comment

Enantiomers do not differ in their physical and chemical properties, but could differ in their physiological mode of action [7]. Therefore crystal structures of chiral amines or hydrochlorides thereof are almost exclusively related to investigations prior to pharmacological use. However, enantiomeric pure chiral amines or the related aminium ions may also serve as chiral building blocks for the construction of chiral supramolecular hydrogen-bonded networks in crystal engineering. Surprisingly, only very few crystal structures of carbon-based chiral primary amine hydrochlorides $[R^*\text{–}NH_3]Cl$ are known so far, namely (*S*)-(−)-1-(4-methylphenyl)ethylammonium chloride [8], (*S*)-α-methylbenzylammonium chloride [9] and rimantadine hydrochloride [10]. Herein we present the crystal structure of the 'chiral salt' (*S*)-(+)-1-cyclohexylethylaminium chloride that exhibits a ladder-shaped hydrogen-bonded double chain combined with a 'ladder in the tube' structure motif based on the surrounding organic substituents.

The title compound crystallizes in the noncentrosymmetric space group $P2_12_12_1$. The absolute structure is given by synthesis based on the corresponding amine, (*S*)-(+)-1-cyclohexylethylamine. The asymmetric unit of the crystal structure is defined by one (*S*)-(+)-1-cyclohexylethylaminium cation and one chloride anion. In the protonated amine moiety the bond lengths N1—C1 1.496(2) Å, C1—C2 1.526(3) Å, and C1—C3 1.535(2) Å as well as the angles at C1 are as expected [11]. The cyclohexyl group of the cation is present in the energetically most favourable conformation, the chair conformation [12]. The C—C bonds in the group have bond lengths of 1.514(3) Å to 1.536(3) Å with an average length of 1.524(3) Å, which is close to the reference value of 1.535(16) Å for C(sp^3)–C(sp^3) bonds in cyclohexyl groups [11]. In correspondence with the values given by Bastiansen et al. (gas phase ED of C_6H_{12}, [13]) and Kahn et al. (crystal structure analysis of C_6H_{12}-II [14]), the C—C—C bond angles in the six-membered ring vary from 110.17(15)° to 112.02(16)°, averaging to 111.10(16)° ([13]: 111.4°; [14]: 111.34°). The torsion angles in the cyclohexyl group range from 54.6(3)° to 57.4(2)° with an average value of 55.8(2)°, which is in good agreement with the calculated value of 55.7° [15]. Taking a closer look at the cation's structure, it is obvious that C5—C6 is shorter and C3—C4 is longer than the average bond length in the cyclohexyl moiety. This is the only feature that might be attributed to the asymmetry of the chiral ethylaminium 'substituent' in equatorial position. However, the difference is at the border of significance and the torsion angles C1—C3—C4—C5 [177.85(15)°] and C1—C3—C8—C7 [177.56(16)°] do not seem to be different, in both cases indicating a nearly staggered conformation. The NH_3 group of the cation is engaged in N—H···Cl type hydrogen bonds to the neighbouring Cl^- ions and each anion serves as an acceptor for two further hydrogen bonds. The N···Cl distances range from 3.1529(16) to 3.1650(17) Å and the hydrogen bond angles from 163(2) to 176(3)°. According to the bond valence method [16] these hydrogen bonds have to be characterized as moderately strong. As shown in the upper part of the figure, altogether the hydrogen bonds form a double-chain hydrogen bond system propagating along the *a* axis of the unit cell that is similar to the system found in (*S*)-(−)-1-(4-methylphenyl) ethylammonium chloride [8]. Note the graph set symbols [17] of the two hydrogen bond motifs defining this ladder-like structure. Projected along the chain propagation direction the lower part of the figure shows a packing diagram indicating the arrangement of the double-chains (blue) according to a moderately distorted hexagonal pattern. Around each of the double-chains a closed surrounding of organyl groups can be recognized that reminds of a tube (red). Each organyl group is part of three neighbouring tubes, giving a pattern of interpenetrating tubular 'organic' sections visualized by the different red areas in the figure. We suppose that this 'ladder in the tube'-structure with its tightly interlocking organic groups is responsible for the unexpected high thermal stability (m. p. 521 K) in comparison to other classes of organylammonium chlorides.

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References

1. Sheldrick, G. M.: SHELXT – integrated space-group and crystal-structure determination. Acta Crystallogr. **C71** (2015) 3–8.
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
3. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Ver. 4.0. Crystal Impact, Bonn, Germany (2014).
4. Hesse, M.; Meier, H.; Zeeh, B.: Spektroskopische Methoden in der organischen Chemie. 7th ed. Thieme, Stuttgart, New York (2005).
5. Flack, H. D.: On enantiomorph-polarity estimation. Acta Crystallogr. **A39** (1983) 876–881.
6. Hooft, R. W. W.; Straver, L. H.; Spek, A. L.: Determination of absolute structure using Bayesian statistics on Bijvoet differences. J. Appl. Crystallogr. **41** (2008) 96–103.
7. Fassihi, A. R.: Racemates and enantiomers in drug development. Int. J. Pharm. **92** (1993) 1–14.
8. Hernández, G.; Bernès, S.; Portillo, R.; Gutiérrez, R.: (*S*)-(−)-1-(4-Methylphenyl)ethylammonium chloride. Acta Crystallogr. **E63** (2007) o1053–o1055.
9. Ben Salah, A. M.; Naïli, H.; Mhiri, T.; Bataille, T.: Synthesis and crystal structure of a chiral aromatic amine chloride salt ($C_8H_{12}N$)Cl. Crystallogr. Rep. **60** (2015) 1053–1057.
10. Mishnev, A.; Stepanovs, D.: Crystal structure explains crystal habit for the antiviral drug rimantadine hydrochloride. Z. Naturforsch. B **69** (2014) 823–828.
11. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R.: Tables of bond lengths determined by X-ray and neutron diffraction. part 1. bond lengths in organic compounds. J. Chem. Soc., Perkin Trans. 2 **12** (1987) 1–19.
12. Johnson, W. S.; Bauer, V. J.; Margrave, J. L.; Frisch, M. A.; Dreger, L. H.; Hubbard, W. N.: The energy difference between the chair and boat forms of cyclohexane. the twist conformation of cyclohexane. J. Am. Chem. Soc. **83** (1961) 606–614.
13. Bastiansen, O.; Fernholt, L.; Seip, H. M.; Kambara, H.; Kuchitsu, K.: Structure of cyclohexane determined by two independent gas electron-diffraction investigations. J. Mol. Struct. **18** (1973) 163–168.
14. Kahn, R.; Fourme, R.; André, D.; Renaud, M.: Crystal structures of cyclohexane I and II. Acta Crystallogr. **B29** (1973) 131–138.
15. Geise, H. J.; Buys, H. R.; Mijlhoff, F. C.: Conformation of non-aromatic ring compounds: part 72. an electron diffraction study of gaseous cyclohexane and methylcyclohexane. J. Mol. Struct. **9** (1971) 447–454.
16. Brown, I. D.: Recent developments in the methods and applications of the bond valence model. Chem. Rev. **109** (2009) 6858–6919.
17. Etter, M. C.; MacDonald, J. C.; Bernstein, J.: Graph-set analysis of hydrogen-bond patterns in organic crystals. Acta Crystallogr. **B46** (1990) 256–262.