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Quininium (*S*)-2-chloro-*n*-butyrate

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Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.105
Data-to-parameter ratio = 14.1

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

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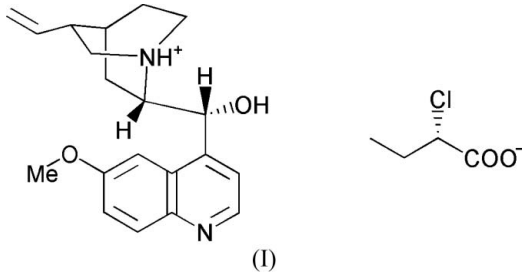
The title compound, $C_{20}H_{25}N_2O_2^+\cdot C_4H_6ClO_2^-$, was crystallized by evaporation of an acetone solution and this is the first published report describing the structure of a crystal phase for this salt. Quinine is commonly used as a resolving agent for classic resolution. The anion was of interest because it has several desirable properties for absolute configuration studies, *viz*. strong acidic pK_a for salt formation, a somewhat heavy atom for strong diffraction and a known stereocenter.

Comment

As part of a study of counter-ions for absolute configuration determination, we solved the crystal structure of the title salt, (I), at 299 K (Fig. 1).



(I)

The asymmetric unit of (I) contains one quininium cation (protonated at the tertiary amine) and one butyrate anion (deprotonated at the carboxylic acid). The space group $P4_32_12$ was identified from the systematic absences. The Flack (1983) parameter was 0.00 (11), just outside the range of strong distinguishing power for absolute configuration (Flack & Bernardinelli, 2000). The structure is consistent with the expected configuration for both parts of the salt.

The bond lengths in the acid group of the counter-ion are consistent with a carboxylate. The acidic H atom was located on the amine group of the free quinine and is significant in the hydrogen bonding. The structure has six hydrogen-bond acceptors and only two hydrogen-bond donors, both of which are used in the hydrogen-bonding network. The typically strongest acceptors are hydrogen bound (carboxylate), while the typically weaker acceptors are not (OMe, OH, aromatic N) (Fig. 2).

Within the unit cell are chains of quininium cations linked by O—H···O and N—H···O hydrogen bonds. These chains are linked across the butyrate anions through the carboxylate group along all three axes (Table 1).

Experimental

Stock solutions of quinine and (*S*)-2-chloro-*n*-butyric acid were made in acetone at concentrations of approximately 1 mg ml^{-1}. The stock

solutions were added together in a crystallization block made of polyethylene and pressed against a smooth glass plate. The solution was left to evaporate and the glass plate was separated from the crystallizer block. A columnar crystal was removed from the plate and mounted on a glass fiber for data collection.

Crystal data

$C_{20}H_{25}N_2O_2^+\cdot C_4H_6ClO_2^-$
M_r = 446.96
Tetragonal, $P4_32_12$
a = 10.5135 (5) Å
c = 41.618 (3) Å
V = 4600.2 (5) Å^3
Z = 8
D_x = 1.291 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1003 reflections
θ = 2.0–25.5°
μ = 0.20 mm^{-1}
T = 299 (2) K
Column, colorless
0.38 × 0.38 × 0.33 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.835, T_{max} = 0.937
32606 measured reflections
4091 independent reflections
3651 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 25.5°
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -45 \rightarrow 49$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.105
S = 1.09
4091 reflections
290 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 2.0903P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 1587 Friedel pairs
Flack parameter: 0.00 (11)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H99B···O3^{i}	0.84 (4)	1.98 (4)	2.786 (3)	162 (4)
N1—H99A···O4^{ii}	0.95 (3)	2.54 (3)	3.299 (3)	137 (2)
N1—H99A···O3^{ii}	0.95 (3)	1.82 (3)	2.718 (3)	158 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{1}{4}$.

H atoms bonded to N and O atoms were located in a Fourier difference map and refined with U_{iso}(H) = 1.2U_{eq}(N) and U_{iso}(H) = 1.5U_{eq}(O). The bond lengths were restrained to 0.86 (2) Å (NH) and 0.91 (2) Å (OH). H atoms bonded to C atoms were placed in calculated positions and treated as riding on their parent atoms, with displacement parameters fixed at U_{iso}(H) = 1.5U_{eq}(carrier atom) for methine and methyl groups, and U_{iso}(H) = 1.2U_{eq}(carrier atom) for methylene groups. C—H bond lengths were constrained to 0.93–0.98 Å.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL*.

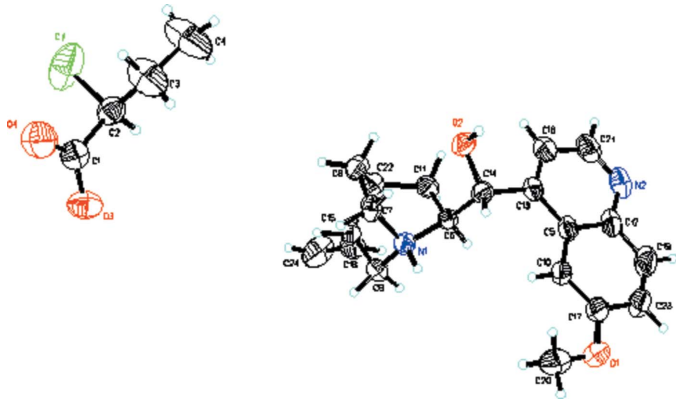


Figure 1
View of the structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

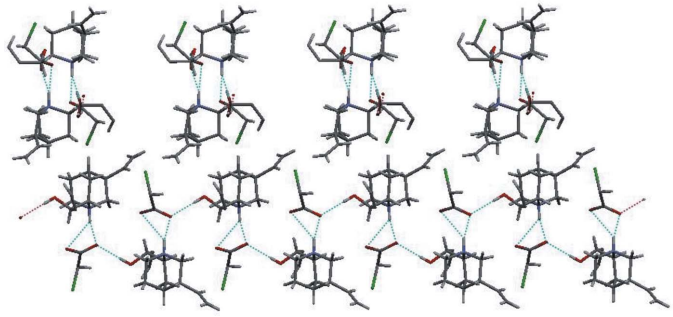


Figure 2
The hydrogen-bonding network looking down on to [010]. Some atoms have been omitted for clarity.

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