L-Leucinium perchlorate

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Crystals of L-leucinium perchlorate, $C_6H_{14}NO_2^+ \cdot ClO_4^-$, are built up from protonated L-leucinium cations and perchlorate anions. L-Leucinium cations related by a twofold screw axis are interconnected by $N-H \cdots O$ hydrogen bonds into zigzag chains parallel to [010]. The O atoms of the perchlorate anions act as acceptors of hydrogen bonds that link the L-leucinium chains into separated but interacting two-dimensional layers parallel to (001). Since the title compound crystallizes in a non-centrosymmetric space group, it can be useful as a material for non-linear optics. The efficiency of second harmonic generation is about twice that of $K_2[HPO_4]$.

Comment

The present study is a continuation of our investigations characterizing the hydrogen-bonding system in the solid state of materials that generate SHG (second harmonic generation) (Janczak & Perpétuo, 2002; Marchewka et al., 2003; Perpétuo & Janczak, 2006). In order to expand understanding of the solid-state physical–organic chemistry of compounds for non-linear optics, we investigate here the solid-state structure of L-leucinium perchlorate, (I). Additionally, the geometries of the oppositely charged units of the crystal, i.e. the protonated L-leucinium cation and the perchlorate anion, are compared with ab initio optimized parameters calculated at the B3LYP/6-31G(d) level (Frisch et al., 1998) and the results are shown in Fig. 1.
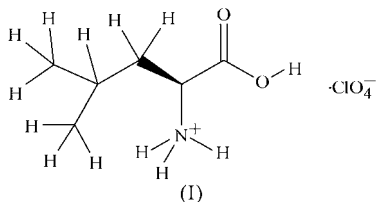
The asymmetric unit of (I) consists of a protonated L-leucinium cation and a perchlorate anion (Fig. 2). The protonated L-leucinium cation adopts an extended conformation, where the methyl groups are at a maximum distance from the polar groups, making the C—C bonds (Table 1)

slightly longer than a typical single C—C bond [1.515 (5) Å; Allen et al., 1987]. The steric effect and interaction between the two methyl groups and both polar NH_3^+ and COOH groups makes the C2—C3—C4 angle larger than the remaining C—C—C angles within the L-leucinium skeleton. The protonated amine group interacts with the polar COOH group, making the C1—C2—N1 angle slightly smaller than the tetrahedral value of 109.5°. The correlations between the values of the C—C bond lengths and C—C—C angles within the skeleton are more pronounced in the ab inito optimized geometry of the L-leucinium cation. The extended conformation of the L-leucinium cation is described well by the orientation of the polar NH_3^+ and COOH groups in relation to the carbon skeleton.

The orientation of the NH_3^+ group is almost coplanar with the C2—C3—C4—C6 chain [the N1—C2—C3—C4 and C2—C3—C4—C6 torsion angles are −170.6 (2) and −177.5 (2)°, respectively], while the COOH group and the other methyl group (C5) deviate significantly from this skeleton plane [the C1—C2—C3—C4 and C5—C4—C3—C2 torsion angles are 70.0 (2) and 60.9 (2)°, respectively]. A similar extended conformation of the skeleton is observed in the crystal structure of L-leucine (Coll et al., 1986; Görbitz & Dalhus, 1996) and in almost all the known crystals of L-leucine with organic or inorganic acids (Allen, 2002), except for L-leucinium oxalate (Rajagopal et al., 2003) and L-leucine L-leucinium
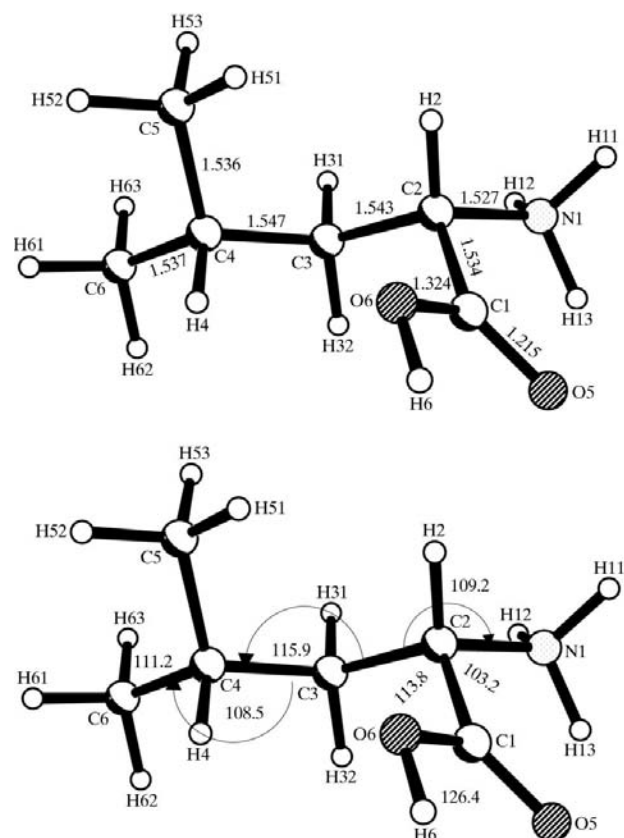

Figure 1
Results of optimized molecular orbital calculations for the L-leucinium cation. Bond lengths are given in Angstroms (Å) and angles are given in degrees (°).

organic compounds

picrate (Anitha *et al.*, 2005), in each of which the C atom of the carboxyl group is almost coplanar with the C2—C3—C4—C6 skeleton.

The perchlorate anion shows noticeable distortion from the tetrahedral geometry predicted by the *ab initio* optimization (Cl—O = 1.499 Å and O—Cl—O = 109.49°); firstly, the observed Cl—O bonds are different [1.389 (2)–1.413 (2) Å] and, secondly, the O—Cl—O angles are not equivalent, ranging from 106.7 (2) to 115.7 (2)°. The distortion of the ClO_4^- ion from T_d symmetry is most likely due to the different interactions of the O atoms with the L-leucinium cations that act as acceptors in the hydrogen bonds.

In the crystal structure, the L-leucinium cations related by a twofold screw axis interact *via* N—H···O hydrogen bonds, forming infinite zigzag chains parallel to the *b* axis. The O atoms of the perchlorate anion as acceptors of hydrogen bonds interconnect the translationally equivalent chains of L-leucinium cations into two-dimensional layers perpendicular to the *c* axis (Fig. 3). Within the layers, the N—H···O interaction between the L-leucinium cations and the interionic interactions between the L-leucinium(+) and ClO_4^- ions (N—H···O and O—H···O) are stronger than that between the

layers. There are no direction-specific interactions between adjacent sheets, accounting for the marked cleavage properties of the crystals, but the isobutyl groups of L-leucinium units in adjacent sheets are interdigitated (Fig. 2).

Two H atoms of the protonated amine group are each involved in two N—H···O hydrogen bonds, while the third forms one N—H···O bond (see Table 2). Besides these N—H···O hydrogen bonds, the L-leucinium cation is involved, *via* the OH group, in an O—H···O hydrogen bond with the ClO_4^- anion, which acts as an acceptor in five hydrogen bonds. Atoms O1, O2 and O3 are each acceptors in one hydrogen bond, while atom O4 is involved in two such interactions (Table 2).

The SHG experiment was carried out using the Kutz–Perry powder technique (Kurtz & Perry, 1968). Samples of L-leucinium perchlorate and $K_2[HPO_4]$ (KDP) were irradiated at 1064 nm by an Nd:YAG laser and the second harmonic beam power diffused by the samples at 532 nm was measured as a function of the fundamental beam power. SHG efficiency for L-leucinium perchlorate is about two times larger than for KDP [$d_{eff} \simeq 2d_{eff}(KDP)$].

Figure 2
A view of the molecular structure of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii.

Figure 3
The crystal packing, viewed approximately along [100], showing three (001) sheets and their interdigitated isobutyl groups. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Experimental

L-Leucine was dissolved in 10% aqueous perchloric acid; after several days, colourless single crystals had formed, which proved to be suitable for single-crystal X-ray diffraction analysis.

Crystal data

$C_6H_{14}NO_2^+ \cdot ClO_4^-$	$D_x = 1.455$ Mg m^{-3}
$M_r = 231.63$	$D_m = 1.45$ Mg m^{-3}
Monoclinic, $P2_1$	D_m measured by flotation
$a = 5.640$ (1) Å	Mo $K\alpha$ radiation
$b = 8.768$ (2) Å	$\mu = 0.37$ mm^{-1}
$c = 10.704$ (2) Å	$T = 295$ (2) K
$\beta = 92.49$ (3)°	Parallelepiped, colourless
$V = 528.83$ (18) Å^3	$0.28 \times 0.22 \times 0.18$ mm
$Z = 2$	

Data collection

Kuma KM-4 diffractometer with a CCD area-detector	6261 measured reflections
	2599 independent reflections
ω scans	1972 reflections with $I > 2\sigma(I)$
Absorption correction: analytical (face-indexed; *SHELXTL*; Sheldrick, 1990)	$R_{int} = 0.020$
	$\theta_{max} = 28.6°$
$T_{min} = 0.915$, $T_{max} = 0.941$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
2599 reflections	$\Delta\rho_{min} = -0.30$ e Å^{-3}
131 parameters	Absolute structure: Flack (1983), 1162 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.13 (8)

All H atoms were treated as riding atoms, with C—H distances of 0.96–0.98 Å, N—H distances of 0.89 Å and O—H distances of 0.82 Å, and with $U_{iso}(H)$ set equal to $kU_{eq}(C,N,O)$, where $k = 1.5$ for methyl, ammonium and OH groups, and $k = 1.2$ for all other H atoms. In the absence of significant resonance scattering, the Friedel-equivalent reflections were merged; the absolute structure was assigned from the known configuration of the leucine component.
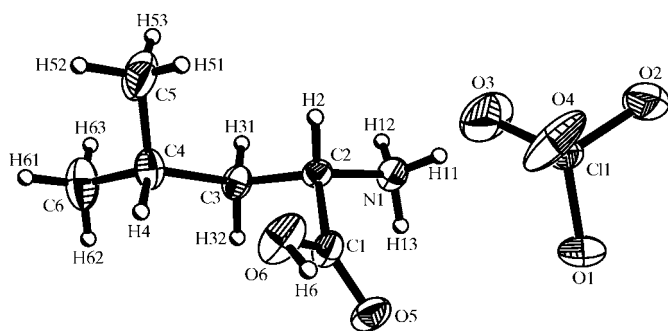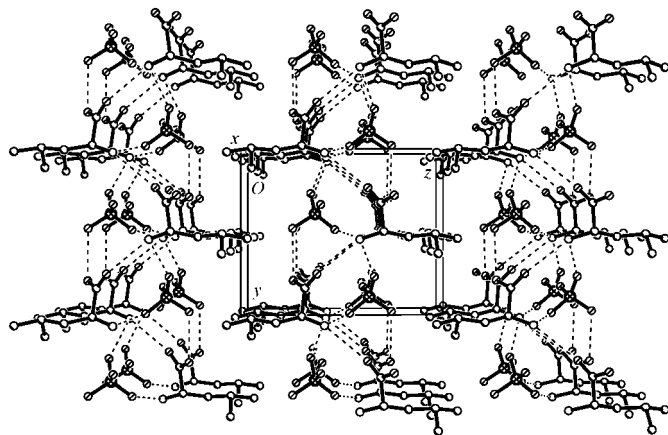
Table 1
Selected geometric parameters (Å, °).

Cl1—O3	1.389 (2)	C1—C2	1.491 (4)
Cl1—O4	1.390 (3)	C2—N1	1.492 (3)
Cl1—O2	1.412 (3)	C2—C3	1.537 (4)
Cl1—O1	1.413 (2)	C3—C4	1.521 (4)
O5—C1	1.205 (3)	C4—C5	1.525 (5)
O6—C1	1.310 (3)	C4—C6	1.532 (4)
O3—Cl1—O4	106.7 (2)	O4—Cl1—O1	108.55 (19)
O3—Cl1—O2	109.1 (2)	O2—Cl1—O1	109.40 (15)
O4—Cl1—O2	107.0 (3)	O5—C1—O6	124.0 (3)
O3—Cl1—O1	115.71 (16)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H11$\cdots$O3	0.89	2.21	2.939 (4)	139
O6—H6$\cdots$O2^{i}	0.82	2.12	2.746 (3)	133
N1—H12$\cdots$O1^{ii}	0.89	2.16	2.954 (3)	149
N1—H12$\cdots$O4^{iii}	0.89	2.57	2.995 (4)	110
N1—H13$\cdots$O4^{iv}	0.89	2.36	3.041 (4)	134
N1—H11$\cdots$O5^{ii}	0.89	2.45	2.852 (3)	108

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

Data collection, cell refinement and data reduction: *KM-4 CCD Software* (Kuma, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); publication material: *SHELXL97*.

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