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DL-Leucinium nitrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.093
Data-to-parameter ratio = 23.6

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

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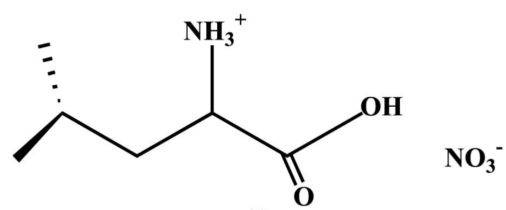
The crystal structure of DL-2-ammonium-4-methylvaleric acid nitrate ($C_6H_{14}NO_2^+\cdot NO_3^-$, DL-leucinium nitrate) can be described by considering two types of layers parallel to the *bc* plane: hydrophilic layers including the head of the leucinium residue (ammonium and carboxylic groups) with the nitrate anion, and hydrophobic layers including the tail of the leucinium residue.

Comment

The interesting electrical, magnetic or optical properties (Kagan *et al.*, 1999; Hill, 1998) that hybrid compounds can exhibit, as well as their richness of hydrogen bonds, explains the great interest in these compounds in recent years (Mazeaud *et al.*, 2000; Soghomonian *et al.*, 1995; Mayer *et al.*, 1999; Siegel *et al.*, 1998; Baker *et al.*, 1992).



(I)

The present work is a continuation of the research that we have undertaken on the synthesis and crystal structures of new hybrid compounds to study the nature of hydrogen bonding and interactions between various organic cations and inorganic acids (nitric, phosphoric and sulfuric acids) in their crystalline forms (Benali-Cherif *et al.*, 2004; Berrah *et al.*, 2005; Cherouana *et al.*, 2003; Benali-Cherif *et al.*, 2002).

Leucine, like isoleucine and valine, is a hydrophobic branched-chain amino acid that is found as a structural element in the interior of proteins and enzymes (only the L-stereoisomer appears in mammalian protein). There appears to be no other significant metabolic role for these amino acids, but they are essential and, because they are not synthesized by mammalian tissues, must be taken in the diet.

The triclinic structure of L-leucinium nitrate was determinated by Bahadur *et al.* (1993), and in the present paper, we describe the monoclinic structure of DL-leucinium nitrate, (I).

The asymmetric unit of (I) is shown in Fig. 1. Hydrogen bonds are observed between the leucinium cation and the nitrate anion (O2—H6···O3), within the leucinium cation (C4—H8···O2 and C6—H6*A*···O2), and between the amino group and three neighbouring molecules (Table 2).

The torsion angles in (I) and the corresponding angles in L-leucine, (II) (Görbitz & Dalhus, 1996), and L-leucinium

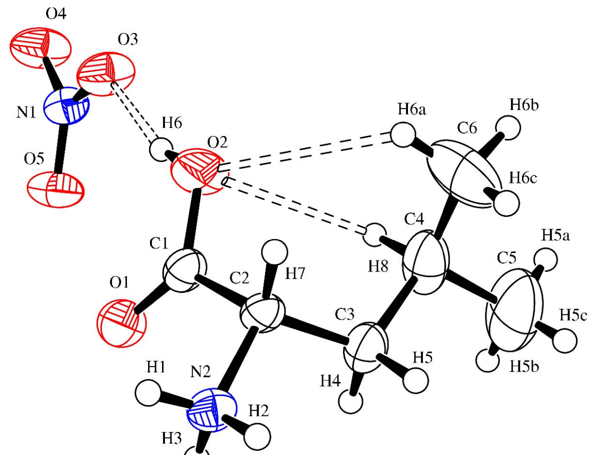


Figure 1
ORTEP-3 (Farrugia, 1997) view of the asymmetric unit of the title compound, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent hydrogen bonds.

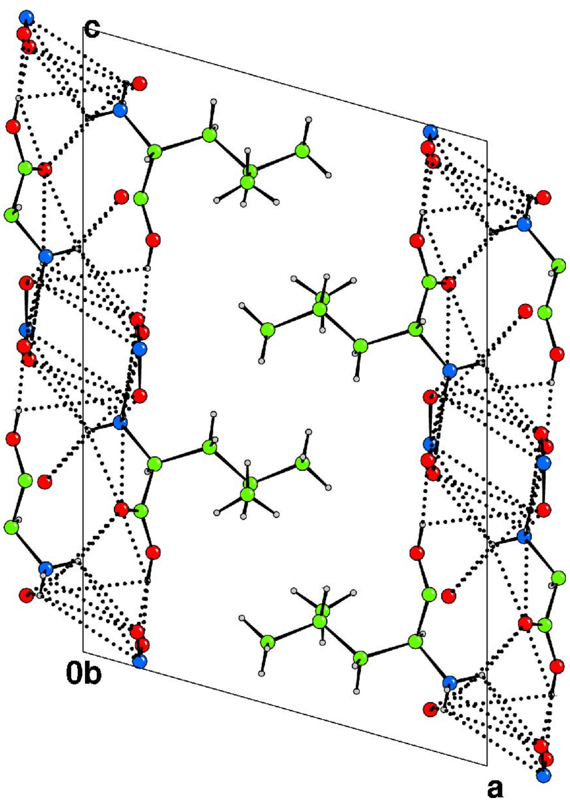


Figure 2
Packing view (*CAMERON*; Watkin *et al.*, 1993) of (I), showing hydrophilic and hydrophobic double layers. Dotted lines represent hydrogen bonds.

nitrate, (III), are similar (Table 3); for example, the torsion angle describing the backbone conformation (O1—C1—C2—N2) is −27.18 (19)° in (I), −26.75 (13) and −32.28 (13)° in (II), and 33.22 (12) and 29.93 (11)° in (III). This similarity shows that the leucine molecule and the leucinium cation take up roughly the same conformation in these three compounds. The bond distances and angles of the leucinium residue in (I) (Table 1) are also in agreement with those observed in (II) and (III).

The molecular packing arrangement adopted in (I) was previously observed in other compounds, such as L-leucine, L-leucinium nitrate, glycyl-DL-leucine (Bombicz *et al.*, 2000) and D-phenylglycinium nitrate (Bouchouit *et al.*, 2004). The packing consists of two types of double layers stacked alternately along the *a* axis (Fig. 2), *viz.* hydrophilic layers at $x = 0$ and hydrophobic layers at $x = \frac{1}{2}$. The hydrophilic layers include the head of the leucinium residue (ammonium and carboxylic groups) and the nitrate anion. A complex system of hydrogen bonds ensures the cohesion of these layers. Inside the hydrophobic layers, which include the tail of the leucinium residue, the aliphatic chain remains free. This fact may explain the large U_{eq} observed for the C atoms of the two methyl groups, 0.0951 (8) Å^2 for C5 and 0.0969 (8) Å^2 for C6.

Experimental

Compound (I) was crystallized by the slow evaporation of an aqueous solution of DL-leucine and nitric acid in a 1:1 stoichiometric ratio.

Crystal data

$C_6H_{14}NO_2^+ \cdot NO_3^-$	$D_x = 1.316$ Mg m^{-3}
$M_r = 194.19$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 10 828 reflections
$a = 11.0324$ (2) Å	$\theta = 5.9$–30.0°
$b = 5.6200$ (2) Å	$\mu = 0.11$ mm^{-1}
$c = 16.4317$ (3) Å	$T = 293$ (2) K
$\beta = 105.789$ (2)°	Block, colourless
$V = 980.36$ (4) Å^3	0.30 × 0.15 × 0.10 mm
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{int} = 0.094$
φ scans	$\theta_{max} = 30.0°$
10 828 measured reflections	$h = -15 \rightarrow 15$
2829 independent reflections	$k = -7 \rightarrow 7$
1319 reflections with $I > 2\sigma(I)$	$l = -23 \rightarrow 21$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.093$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.84$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
2829 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
120 parameters	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2037 (15)	C1—C2	1.5097 (19)
O2—C1	1.3083 (17)	C2—C3	1.526 (2)
O3—N1	1.2698 (13)	C3—C4	1.515 (2)
O4—N1	1.2455 (14)	C4—C6	1.520 (2)
O5—N1	1.2200 (14)	C4—C5	1.523 (3)
N2—C2	1.4783 (17)		
O5—N1—O4	121.81 (11)	N2—C2—C3	108.67 (11)
O5—N1—O3	121.06 (12)	C1—C2—C3	112.28 (12)
O4—N1—O3	117.13 (11)	C4—C3—C2	116.08 (14)
O1—C1—O2	125.49 (13)	C3—C4—C6	111.54 (15)
O1—C1—C2	123.02 (13)	C3—C4—C5	109.35 (17)
O2—C1—C2	111.48 (12)	C6—C4—C5	111.42 (18)
N2—C2—C1	108.24 (11)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H6···O3^{i}	0.89	1.75	2.617 (1)	162
C2—H7···O4^{ii}	1.03	2.51	3.102 (2)	116
C4—H8···O2^{i}	1.02	2.56	3.146 (2)	116
C5—H5*A*···O5^{iii}	0.96	2.81	3.448 (2)	125
C6—H6*A*···O2^{i}	0.96	2.83	3.439 (2)	122
N2—H1···O5^{iv}	0.88	2.43	2.913 (2)	115
N2—H1···O1^{iv}	0.88	2.14	2.865 (1)	139
N2—H2···O4^{ii}	0.87	2.45	3.041 (1)	126
N2—H2···O3^{ii}	0.87	2.01	2.885 (1)	177
N2—H3···O5^{v}	0.86	2.78	3.349 (2)	125
N2—H3···O4^{v}	0.86	1.99	2.840 (1)	171

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

Table 3
Comparison of torsion angles (°) in L-leucine and DL and L forms of leucinium.

Torsion angle	(I)	(II)	(III)
O1—C1—C2—N2	−27.18 (19)	−26.75 (13)/−32.28 (13)	33.22 (12)/29.93 (11)
C2—C3—C4—C6	59.81 (19)	64.63 (13)/71.00 (15)	−59.29 (9)/−58.82 (9)
C2—C3—C4—C5	−176.49 (14)	−174.29 (12)/−166.89 (14)	176.89 (7)/176.69 (7)
N2—C2—C3—C4	−176.47 (11)	−176.81 (10)/−170.01 (11)	175.10 (7)/177.66 (7)
C1—C2—C3—C4	63.83 (16)	63.33 (13)/69.86 (16)	−64.90 (9)/−62.74 (9)

Notes: (I) title compound; (II) L-leucine; (III) L-leucinium nitrate.

All H atoms were located in difference Fourier maps. Methyl H atoms were refined as an idealized methyl group, with C—H = 0.96 Å and with $U_{iso}(H) = 1.5U_{eq}(C)$. The remaining H atoms were refined as riding [N—H = 0.86–0.88 Å, C—H = 0.98–1.04 Å and $U_{iso}(H)$ = 0.05 Å^2].

Data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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