

Strong hydrogen-bonded amino acid dimers in L-alanine alaninium nitrate

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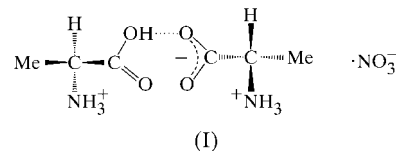
The title compound, $C_3H_7NO_2 \cdot C_3H_8NO_2^+ \cdot NO_3^-$, contains L-alanine–alaninium dimers bonded *via* the carboxyl groups by a strong asymmetric hydrogen bond with an O...O distance of 2.4547 (19) Å. The neutral alanine molecule exists as a zwitterion, where the carboxyl group is dissociated and the amino group is protonated. The alaninium cation has both groups in their acidic form. The alanine molecule and the alaninium cation differ only slightly in their conformation, having an N–C_α–C=O torsion angle close to –25°. The dimers and the nitrate anion are joined through a three-dimensional hydrogen-bond network, in which the full hydrogen-bonding capabilities of the amino groups of the two alanine moieties are realised.

Comment

Diglycine nitrate (DGN) is one of the few glycine salts which exhibits ferroelectric behaviour. It was first reported by Pepinsky *et al.* (1958) to order below 206 K with a reversible spontaneous polarization parallel to the [101] direction. The dielectric constant measured along this direction shows a sharp anomaly at the Curie point (T_c) and a broad anomaly in the specific heat in the temperature range 193–204 K. A number of structural and spectroscopic studies of this compound have been reported (Sato, 1968; Rodin *et al.*, 1988; Lukaszewicz *et al.*, 1996*a,b*; Baran *et al.*, 1994, 1995), aiming to unravel the mechanism responsible for the ferroelectric order. In the high-temperature phase, the structure is centrosymmetric ($P2_1/a$), with pairs of glycinium ions and glycine molecules joined by a strong asymmetric hydrogen bond between the carboxyl groups. Low-temperature X-ray diffraction data showed that the 2_1 screw axis present in the paraelectric phase disappears at the Curie temperature. The nitrate ions were found to be highly disordered in the paraelectric phase, this disorder being much reduced when the crystal enters the ferroelectric phase, as a result of an enhanced N–H...O interaction between the nitrate anions and the NH_3^+ groups of neighbouring glycine cations. The hydrogen bond that links the glycine–glycinium dimers becomes more asymmetric

below T_c , but on the basis of spectroscopic data, it was concluded that the proton motion in the O...H...O bond does not play a major role in the phase transition (Baran *et al.*, 1995).

Looking for new materials with ferroelectric properties, we have synthesized the title compound, L-alanine alaninium nitrate, (I). Alanine is the next highest homologue of glycine, one of the H atoms on the α -C having been replaced by a methyl group. This substitution makes the α -C a chiral centre and this amino acid has optical activity, in contrast with glycine. The methyl side chain is non-polar and moderately hydrophobic. According to a recent survey of the Cambridge Structural Database (release October 2000; Allen & Kennard, 1993), only one occurrence was found of a crystal structure of a 2:1 salt of alanine with an inorganic acid, namely, that of bis(DL-alanine) phosphate (Averbuch-Pouchot *et al.*, 1988). The crystal structures of the 1:1 nitrate salts of L-alanine (Němec, Císařová & Mička, 1999), DL-alanine (Bahadur & Rajaram, 1995) and β -alanine (Němec, Gyepes & Mička, 1999) have already been reported.



The crystal structure of (I) consists of dimers of L-alanine–alaninium counterbalanced by nitrate ions (Fig. 1). The ionization states of the amino acid molecules were determined by the objective localization of the H atoms in a Fourier difference synthesis, and were found to agree with the observed variation of the C–O bond distances.

The neutral alanine molecule exists as a zwitterion, where the carboxyl group is dissociated (COO^-) and the amino group is protonated (NH_3^+). In the cationic form of alanine (alaninium), both groups are in the acidic form. The carboxyl H atom is shared between the cation and the neutral molecule in a strong non-linear asymmetric hydrogen bond, with an O1...O4 distance of 2.4547 (19) Å and a rather short H1...O4 distance of 1.39 (4) Å, which qualifies it as a ‘very strong’ hydrogen bond. As expected for such a strong hydrogen bond, the O1–H1 bond length is stretched compared with the typical value for an hydroxyl bond. The hydrogen bond differs from linearity by 12 (3)°. The carboxyl groups of the two molecules are not coplanar, the angle between the least-squares planes being 28.48 (17)°.

Interestingly, the bridging H atom is *syn* to the donor carboxyl group and *anti* to the dissociated carboxyl group acting as acceptor, as shown by the values of the torsion angles O2=C1–O1–H1 [–4 (3)°] and O3=C4–O4–H1 [174 (2)°]. A dimer with similar characteristics, but with the bridging H atom in a *syn,syn* position, was recently reported in betaine betainium oxalate (betaine is trimethylglycine; Rodrigues *et al.*, 2001).

The two amino acid molecules have similar conformations, bond lengths and valence angles, with the exception of the carboxyl groups. The C–O and C=O bonds not involved in

the intramolecular hydrogen bond are significantly shorter than the other two bonds of this type, and the O—C—O angle of the cation is larger by approximately 3° than that in the neutral molecule. The carboxyl groups are planar and almost perpendicular to the plane defined by the three C atoms, as shown by the torsion angles C3—C2—C1=O2 and C6—C5—C4=O3 of 93.0 (2) and 95.60 (19)°, respectively.

In addition to tautomerism (dipolar–zwitterionic *versus* ‘neutral’ forms), it is known that the L-alanine molecule has some degree of conformational flexibility, due to a relatively low barrier for rotation of the carboxyl group around the central C—C bond. It has been established both experimentally and theoretically that the conformation of the molecule in solution can be influenced by the presence of solvent molecules, through electrostatic interactions and also hydrogen-bond formation (Tajkhorshid *et al.*, 1998). Interestingly, and similarly to glycine, the zwitterionic form of

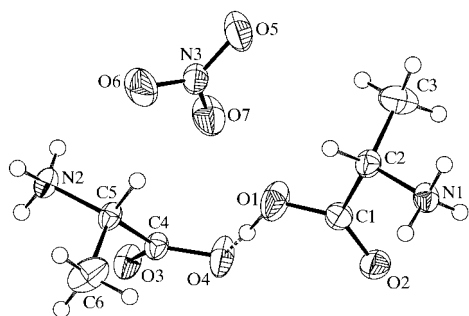


Figure 1

The molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small spheres of arbitrary radii.

L-alanine is not stable for an isolated molecule (Rosado *et al.*, 1997). *Ab initio* calculations have shown that although the zwitterion is stable when neglecting electron correlation in Hartree–Fock models, it becomes unstable and reverts to the non-ionized form when electron correlation is included (Tajkhorshid *et al.*, 1998). However, it is well known that in solution, L-alanine exists as a zwitterion stabilized by electrostatic, polarization and hydrogen-bonding interactions with the solvent molecules. The zwitterionic form is also found in crystalline L-alanine and its adducts or salts in the solid state. *Ab initio* calculations predict that the most stable conformer of the zwitterionic amino acid molecule in a hydrated cluster has the N—C_α—C=O and H—N—C_α—C angles close to 90 and 60°, respectively. This conformation appears to predict satisfactorily the vibrational circular dichroism and the IR and polarized Raman spectra of aqueous alanine solutions (Tajkhorshid *et al.*, 1998). However, an analysis of the available structural data indicates that the N—C_α—C=O torsion angle in the zwitterion seldom exceeds 30° in crystalline compounds, typical values being −18.6° in L-alanine (Destro *et al.*, 1988), 5.1° in L-alaninium chloride (DiBlasio *et al.*, 1977) and 21.9° in DL-alanine nitrate (Bahadur & Rajaram, 1995). In compound (I), this angle is −27.1 (2)° for the cation and −24.6 (2)° for the neutral molecule.

The anion in (I) is planar, as shown by the sum of the internal angles of 360.0 (2)°, but it deviates significantly from ideal *D*_{3h} symmetry. This is not uncommon, due to the sensitivity of the N—O bonds to hydrogen-bonding interactions. The shorter N—O bond corresponds to the O6 atom, which is only involved as an acceptor in one hydrogen bond, whereas atoms O5 and O7 are each acceptors of two hydrogen bonds (see below). Similar and even larger deviations from ideal geometry of the NO₃[−] ion were also observed in DL-alanine nitrate (Bahadur & Rajaram, 1995) and L-alanine nitrate (Němec, Císařová & Mička, 1999). In diglycine nitrate (Lukasiewicz *et al.*, 1996*a,b*), the symmetry of the NO₃[−] ion is close to *D*_{3h} in the paraelectric phase, as determined by spectroscopic methods (Baran *et al.*, 1995), as a result of effectively free rotation, but in the ferroelectric phase, this rotation is inhibited with a consequent lowering of symmetry.

The structure of (I) is held together by a three-dimensional hydrogen-bond network (Fig. 2). The full hydrogen-bonding capabilities of the amino groups of the two alanine molecules are realised. The alanine O atoms that are not already involved in the very strong intra-dimer hydrogen bond accept H atoms from neighbouring NH₃⁺ groups. One of the H atoms bonded to N1 is involved in a bifurcated hydrogen bond towards the lone pairs on O5 and O7 of the same neighbouring nitrate ion. A bifurcated hydrogen bond exists between atoms N2 and O6 of the nitrate ion and O3 of the dissociated carboxyl group of a neighbouring alanine molecule. Geometric details of the hydrogen bonding are given in Table 2. Using hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) to recognize patterns in the three-dimensional network, one finds that N1—H1A···O2ⁱ, N2—H2B···O3^{iv} and N2—H2C···O3^v form, at the unitary level, chains of degree 5 running along the [010] direction [symmetry codes: (i) $-x, \frac{1}{2} + y, 1 - z$; (iv) $1 - x, \frac{1}{2} + y, -z$; (v) $x, 1 + y, z$]. At the basic binary level, the most apparent pattern is the *R*₂¹(4) ring formed by the H1B···(O7—N3—O5)ⁱⁱ···H1B bonds [symmetry code: (ii) $1 - x, \frac{1}{2} + y,$

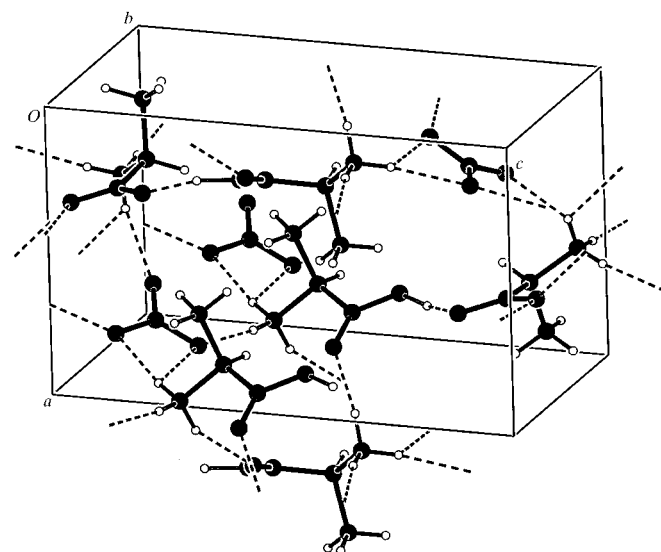


Figure 2

The crystal packing of the molecules of (I), with the hydrogen bonds shown as dashed lines.

1 - z]. At a complex binary level, larger rings are found, the most prominent being H2C—N2—H2B...·(O3—C4—C5—N2—H2B)^{iv}...·O3^v...·H2C with descriptor R₃²(9).

It should be mentioned that because there is no significant anomalous dispersion by any atom of this compound at the Mo K α wavelength, the enantiomorph could not be determined from the X-ray data. Therefore, the well known chirality of L-alanine, where the configuration of the chiral C α atom is S, has been assigned to the molecules. A powder diffraction study between room temperature and 208 (2) K did not disclose any structural phase transition in this temperature range. Measurements of the optical and dielectric properties of this compound are under way.

Experimental

Crystals of (I) were prepared by reacting nitric acid with a dilute aqueous solution of L-alanine (98% purity, Aldrich). Good quality single crystals were grown from the solution by slow evaporation at room temperature over several weeks.

Crystal data

C ₃ H ₇ NO ₂ ·C ₃ H ₈ NO ₂ ⁺ ·NO ₃ ⁻	D _x = 1.463 Mg m ⁻³
M _r = 241.21	Mo K α radiation
Monoclinic, P2 ₁	Cell parameters from 25 reflections
a = 7.8578 (5) Å	θ = 10.2–15.3°
b = 5.4516 (6) Å	μ = 0.13 mm ⁻¹
c = 12.8276 (7) Å	T = 293 (2) K
β = 94.73 (4)°	Plate, colourless
V = 547.63 (8) Å ³	0.42 × 0.37 × 0.12 mm
Z = 2	

Data collection

Enraf–Nonius CAD-4 diffractometer	θ_{\max} = 30°
Profile data from $\omega/2\theta$ scans	h = -10 → 11
2628 measured reflections	k = -7 → 7
1691 independent reflections	l = -18 → 16
1516 reflections with I > 2 σ (I)	3 standard reflections
R _{int} = 0.015	frequency: 180 min
	intensity decay: 10%

Refinement

Refinement on F ²	w = 1/[$\sigma^2(F_o^2) + (0.0446P)^2 + 0.0676P$]
R[F ² > 2 σ (F ²)] = 0.029	where P = (F _o ² + 2F _c ²)/3
wR(F ²) = 0.083	(Δ/σ) _{max} < 0.001
S = 1.10	$\Delta\rho_{\max}$ = 0.28 e Å ⁻³
1691 reflections	$\Delta\rho_{\min}$ = -0.18 e Å ⁻³
169 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.094 (9)

Table 1

Selected geometric parameters (Å, °).

C1—O2	1.218 (2)	N3—O6	1.225 (2)
C1—O1	1.283 (2)	N3—O5	1.247 (2)
C4—O3	1.2344 (19)	N3—O7	1.250 (2)
C4—O4	1.2670 (19)		
O2—C1—O1	126.65 (16)	O6—N3—O7	121.77 (15)
O3—C4—O4	123.79 (16)	O5—N3—O7	118.31 (16)
O6—N3—O5	119.89 (17)		

The coordinates of the H atoms involved in hydrogen bonding were refined freely, with an isotropic displacement parameter proportional to that of the parent atom. Other H atoms were placed at calculated positions and refined as riding using SHELXL97

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O4	1.08 (3)	1.39 (4)	2.4547 (19)	168 (3)
N1—H1A...O2 ⁱ	0.94 (2)	1.92 (2)	2.789 (2)	154 (2)
N1—H1B...O5 ⁱⁱ	0.94 (3)	2.28 (3)	2.861 (2)	119 (2)
N1—H1B...O7 ⁱⁱ	0.94 (3)	2.07 (3)	3.003 (2)	172 (2)
N1—H1C...O5 ⁱⁱⁱ	0.86 (3)	1.99 (3)	2.839 (2)	172 (2)
N2—H2A...O7 ^{iv}	0.89 (3)	2.09 (3)	2.967 (2)	169 (3)
N2—H2B...O6	0.87 (2)	2.14 (2)	2.907 (2)	148 (2)
N2—H2B...O3 ^{iv}	0.87 (2)	2.33 (2)	2.9115 (19)	124.5 (19)
N2—H2C...O3 ^v	0.90 (3)	1.91 (3)	2.8089 (19)	172 (2)

Symmetry codes: (i) -x, ½ + y, 1 - z; (ii) 1 - x, ½ + y, 1 - z; (iii) 1 - x, y - ½, 1 - z; (iv) 1 - x, ½ + y, -z; (v) x, 1 + y, z.

(Sheldrick, 1997) defaults. Examination of the crystal structure with PLATON (Spek, 1997) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: CAD-4 Software (Enraf–Nonius, 1989); cell refinement: CAD-4 Software; data reduction: PLATON; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97; molecular graphics: ORTEPII (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1115). Services for accessing these data are described at the back of the journal.

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