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N-γ-L-Glutamyl-β-cyano-L-alanine, an Antinutritional Factor ex Vicia sativa L., as its Ammonium Salt

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Abstract

The characterization of N-γ-L-glutamyl-β-cyano-L-alanine, an antinutritional factor present in *Vicia sativa* L., as its ammonium salt, $NH_4^+.C_9H_{12}N_3O_5^-$, is reported.

Comment

Seeds of the *Vicia* species are known to contain a wide variety of toxic components, some of which have been implicated as causal agents in human and animal poisoning (Tate & Enneking, 1992). N-γ-L-Glutamyl-β-cyano-L-alanine was first isolated as the major biologically active component from *V. sativa* L. by Ressler, Nigam & Giza (1969). It was shown quantitatively to account for the lethality of diets containing 50% *V. sativa* given to week-old chickens, and higher doses showed growth retardent effects in rats. Tate & Enneking (1992) pointed out the unsuitability of the *V. sativa* cultivar Blanche Fleur (which contains 0.5–0.8% N-γ-L-glutamyl-β-cyano-L-alanine) for human consumption, which at the time was being exported from Australia as a cheap substitute for red lentils (*Lens culinaris*). Subsequently, the importation of dehulled split Blanche Fleur cotyledons was banned by both India and Egypt. The present report details the X-ray structure determination of N-γ-L-glutamyl-β-cyano-L-alanine, characterized as its ammonium salt (I).

(I)
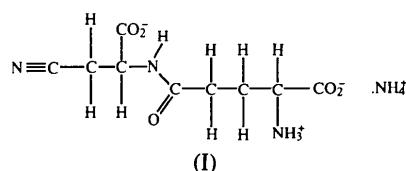
The molecular structure of the anion in (I) is shown in Fig. 1. The end of the molecule possessing the C(1) carboxylate group is zwitterionic with the N(1) atom protonated. The charge balance for the C(7) carboxylate group is provided by the ammonium cation.
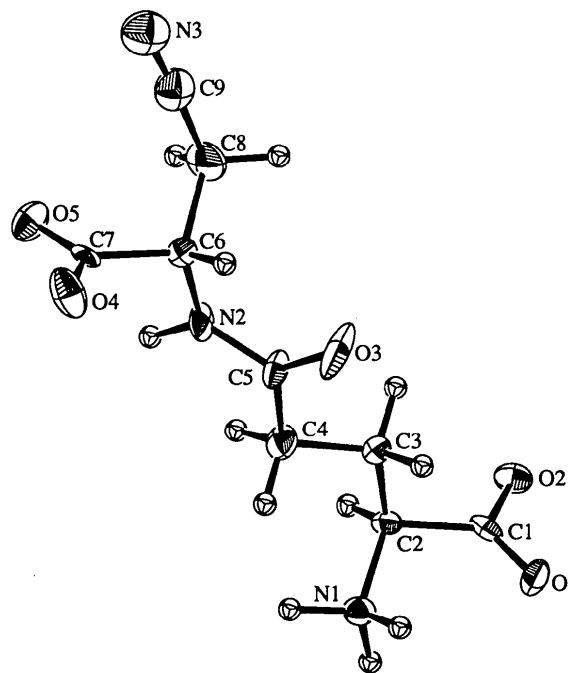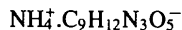

Fig. 1. *ORTEPII* (Johnson, 1976) plot of the molecular structure of the anion in (I) showing 40% probability ellipsoids.

The extended conformation of the main chain C(1–5)—N(2)—C(6)—C(7) is shown clearly in Fig. 1. Similar extended conformations have been found in the crystal structures of glutathione (Görbitz, 1987) and N-γ-L-glutamyl-L-cysteine ethyl ester (Takimoto-Kamimura, Koyano, Kitahara & Fujii, 1990). As expected, there are extensive hydrogen-bonding contacts in the lattice; detailed analysis of these was precluded as the lattice ammonium N(4) H atoms were not located in the X-ray study (contacts are listed in Table 3). The occurrence of three hydrogen-bonding contacts involving the O(2) atom is responsible for the relatively long C(1)—O(2) distance of 1.267 (9) Å.

Experimental

The anion exchange procedure of Ressler *et al.* (1969) was modified by elution with ammonium acetate instead of pyridine. The bulk fractions containing N-γ-L-glutamyl-β-cyano-L-alanine were concentrated to dryness, extracted with methanol to remove ammonium acetate, adjusted to pH 8 with ammonia and crystallized from propanol–water (1:1) solution, yielding crystals suitable for the X-ray study.

Crystal data

$NH_4^+.C_9H_{12}N_3O_5^-$	Mo $K\alpha$ radiation
$M_r = 261.3$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 18
$P2_1$	reflections
$a = 9.347\ (8)$ Å	$\theta = 7.6$–$22.4°$
$b = 4.772\ (7)$ Å	$\mu = 0.123$ mm^{-1}
$c = 12.967\ (5)$ Å	$T = 290$ K
$\beta = 90.49\ (5)°$	Needle
$V = 578.3\ (8)$ Å^3	$0.57 \times 0.08 \times 0.02$ mm
$Z = 2$	Colourless
$D_x = 1.500$ Mg m^{-3}	

Data collection

AFC-6R diffractometer	$R_{int} = 4.65$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction:	$h = 0 \rightarrow 12$
refined from ΔF	$k = 0 \rightarrow 5$
(*DIFABS*; Walker &	$l = -13 \rightarrow 13$
Stuart, 1983)	3 standard reflections
1638 measured reflections	monitored every 400
1548 independent reflections	reflections
698 observed reflections	intensity decay: 0.20%
[$I > 3.0\sigma(I)$]	

Refinement

Refinement on F	Weighting scheme based
$R = 0.060$	on measured e.s.d.'s
$wR = 0.054$	$(\Delta/\sigma)_{max} = 0.001$
$S = 2.08$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
698 reflections	$\Delta\rho_{min} = -0.44$ e Å^{-3}
162 parameters	Atomic scattering factors
H-atom parameters not	from *International Tables*
refined	*for X-ray Crystallography*
	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0.6086 (7)	0.3687	0.4588 (4)	0.030 (3)
O(2)	0.8095 (6)	0.134 (2)	0.4719 (4)	0.030 (3)
O(3)	0.7151 (10)	0.372 (2)	0.0487 (5)	0.060 (4)
O(4)	0.6194 (7)	−0.029 (2)	−0.2528 (5)	0.044 (4)
O(5)	0.7865 (7)	−0.344 (2)	−0.2230 (5)	0.036 (3)
N(1)	0.4857 (8)	−0.028 (2)	0.3447 (5)	0.025 (4)
N(2)	0.7372 (9)	−0.040 (2)	−0.0241 (5)	0.031 (4)
N(3)	1.0382 (9)	0.150 (3)	−0.3075 (6)	0.053 (5)
N(4)	0.1135 (7)	0.122 (2)	0.4261 (5)	0.025 (3)
C(1)	0.688 (1)	0.182 (3)	0.4321 (7)	0.021 (4)
C(2)	0.6420 (9)	−0.006 (3)	0.3428 (6)	0.021 (4)
C(3)	0.6914 (9)	0.134 (3)	0.2436 (6)	0.024 (4)
C(4)	0.642 (1)	−0.017 (3)	0.1466 (6)	0.032 (4)
C(5)	0.700 (1)	0.118 (3)	0.0545 (6)	0.028 (5)
C(6)	0.784 (1)	0.060 (3)	−0.1218 (6)	0.022 (4)
C(7)	0.724 (1)	−0.116 (3)	−0.2074 (6)	0.021 (4)
C(8)	0.948 (1)	0.061 (3)	−0.1228 (7)	0.046 (6)
C(9)	1.000 (1)	0.116 (3)	−0.2243 (8)	0.041 (5)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(1)	1.21 (1)	N(3)—C(9)	1.15 (1)
O(2)—C(1)	1.266 (9)	C(1)—C(2)	1.52 (1)
O(3)—C(5)	1.22 (1)	C(2)—C(3)	1.52 (1)
O(4)—C(7)	1.21 (1)	C(3)—C(4)	1.52 (1)
O(5)—C(7)	1.25 (1)	C(4)—C(5)	1.46 (1)
N(1)—C(2)	1.47 (1)	C(6)—C(7)	1.50 (1)
N(2)—C(5)	1.32 (1)	C(6)—C(8)	1.53 (1)
N(2)—C(6)	1.43 (1)	C(8)—C(9)	1.43 (1)
C(5)—N(2)—C(6)	125.4 (8)	O(3)—C(5)—C(4)	122.2 (8)
O(1)—C(1)—O(2)	124 (1)	N(2)—C(5)—C(4)	118.5 (8)
O(1)—C(1)—C(2)	118.9 (9)	N(2)—C(6)—C(7)	110.6 (8)
O(2)—C(1)—C(2)	116.7 (9)	N(2)—C(6)—C(8)	108.9 (8)
N(1)—C(2)—C(1)	107.6 (7)	C(7)—C(6)—C(8)	111.6 (8)
N(1)—C(2)—C(3)	110.7 (7)	O(4)—C(7)—O(5)	126.6 (10)
C(1)—C(2)—C(3)	107.4 (8)	O(4)—C(7)—C(6)	117.8 (10)
C(2)—C(3)—C(4)	113.5 (8)	O(5)—C(7)—C(6)	115.5 (9)
C(3)—C(4)—C(5)	110.8 (9)	C(6)—C(8)—C(9)	110.8 (8)
O(3)—C(5)—N(2)	119.3 (8)	N(3)—C(9)—C(8)	177 (1)

Table 3. *Contact distances* (Å)

O(1)$\cdots$N(1^i)	2.748 (9)	O(4)$\cdots$N(1^v)	2.83 (1)
O(2)$\cdots$N(4^i)	2.77 (1)	O(4)$\cdots$N(1^{vi})	2.84 (1)
O(2)$\cdots$N(4^{ii})	2.86 (1)	O(5)$\cdots$N(1^v)	3.11 (1)
O(2)$\cdots$N(4^{iii})	2.908 (9)	N(3)$\cdots$N(4^{vi})	3.07 (1)
O(3)$\cdots$N(2^{iv})	2.96 (1)	N(3)$\cdots$N(4^v)	3.27 (1)

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

H atoms were not refined and were assigned the B_{eq} value of the atom to which they were bonded.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond distances and angles involving H atoms, have been deposited with the IUCr (Reference: AS1140). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Comment

The structure determination reported herein forms part of an investigation into the substitution of salts of hydroxylamines, oximes and hydrazones with pentafluoropyridine, in which novel competing 2-substitution was observed in addition to the expected 4-substitution (Banks, Jondi & Tipping, 1989; Jondi, 1989). The structural information was required to confirm that the 4-substituted product was the title oxime (1), and not the alternative immonium oxide (2), which would also aid identification of the 2-substituted product (3), for which crystals suitable for X-ray crystallographic analysis could not be obtained.
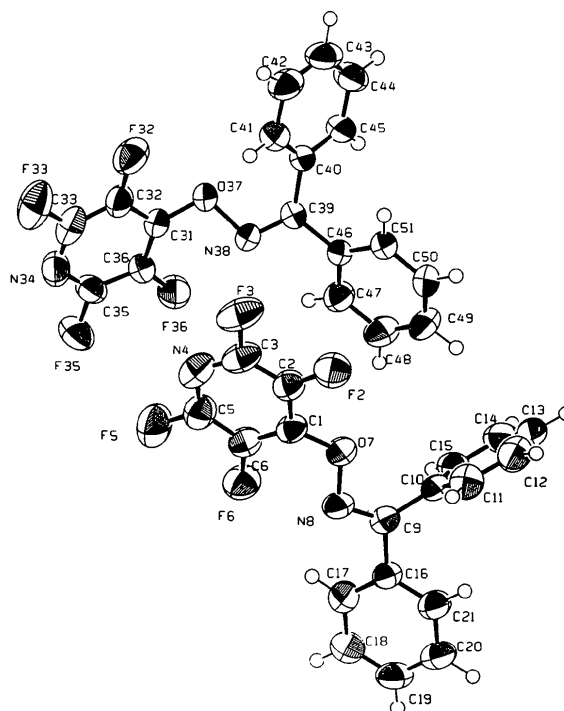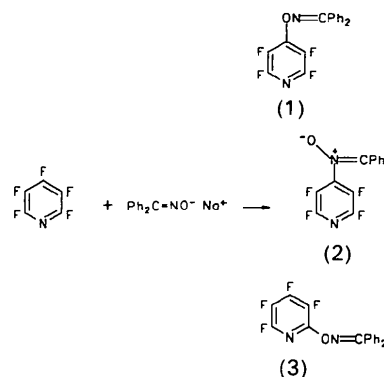
Benzophenone O-(2,3,5,6-Tetrafluoro-4-pyridyl)oxime, Formed by 4-Substitution of Pentafluoropyridine by Benzophenone Oximate

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Abstract

The asymmetric unit of the title compound, $C_{18}H_{10}F_4N_2O$, is composed of two identical molecules having different configurations. Although both molecules adopt a *trans* configuration about the N—O bond [C—N—O—C 164.2 (3) and −162.0 (2)°], substantial twists of all the aromatic rings relative to the C=N—O plane show no correlation between the conformers. Despite the apparently random molecular configurations, the packing arrangement involves several π interactions between adjacent molecules.

Fig. 1. An *ORTEP*II (Johnson, 1976) view of the asymmetric unit of the title compound, comprising two molecules, showing the atomic numbering scheme with ellipsoids set at the 50% probability level.