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DL-Valine NCA

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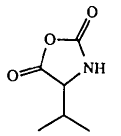
Abstract

The crystal of *N*-carboxy-DL-valine anhydride (DL-valine NCA), $C_6H_9NO_3$, has a similar layer structure to that observed in the crystal of L-valine NCA [Kanazawa, Ohashi & Sasada (1984). *Acta Cryst.* C**40**, 1094–1096]. However, the D and L molecules are connected alternately by N—H···O hydrogen bonds in each layer.

Comment

The *N*-carboxy anhydrides (NCA) of amino acids are useful monomers for the synthesis of polypeptides. These compounds are generally unstable to moisture and heat. A series of studies has been made on crystal structures of these compounds in order to explain their polymerizability in the crystalline state: glycine NCA (Kanazawa *et al.*, 1976*a*), L-alanine NCA (Kanazawa *et al.*, 1976*b*), γ-benzyl-L-glutamate (BLG) NCA (Kanazawa, Ohashi, Sasada & Kawai, 1978*a*), L-leucine NCA (Kanazawa, Ohashi, Sasada & Kawai, 1978*b*) and L-valine NCA (Kanazawa, Ohashi & Sasada, 1984). There are four types of hydrogen bonding in these compounds: the N1···O1 dimer type (glycine NCA), the N1···O1 layer type (L-leucine NCA and L-valine NCA), the N1···O3 type (L-alanine NCA) and the N1···O4 type (BLG NCA). In this paper, the crystal structure of DL-valine NCA, (I), is determined and compared with those of the related compounds.



(I)

The crystals were prepared in a way similar to those of the related compounds. The molecular structure is shown in Fig. 1. Bond distances and angles are consistent with the corresponding ones in L-valine NCA. The bond distances C1—O2 and C2—O2 are in good agreement with those in the N1···O1 dimer and layer-type compounds. This means that O1 is likely to have a negative charge and O2 a positive charge as a result of the resonance in the five-membered ring caused by the intermolecular hydrogen bond (Kanazawa, Ohashi, Sasada & Kawai, 1978*a*). In this case, CO_2 can be readily cleaved from the five-membered ring.

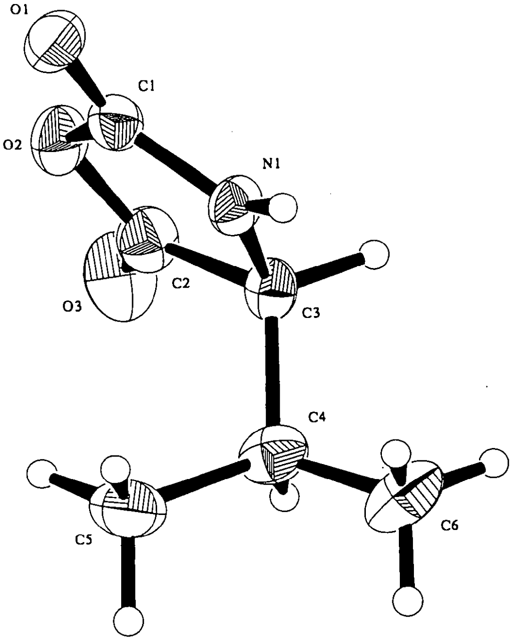


Fig. 1. View of the L isomer of DL-valine NCA showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level, H atoms are drawn as small circles of arbitrary radii.

The crystal structure is shown in Fig. 2. The molecules are connected along the *c* axis by the intermolecular hydrogen bond N1···O1 of 2.935 (6) Å as indicated by dashed lines in Fig. 2. The polymerizing moiety, the five-membered ring, forms a layer structure parallel to the *c* axis and this layer is interwoven with the hydrophobic side-chain layers. Such layer structures are observed in L-leucine NCA and L-valine NCA, *i.e.* the N1···O1 layer-type compounds. The reactivities of

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these compounds are higher than those of the other types of compounds. The hydrogen-bond chain is ordered to DLDL... and different from that of L-valine NCA.

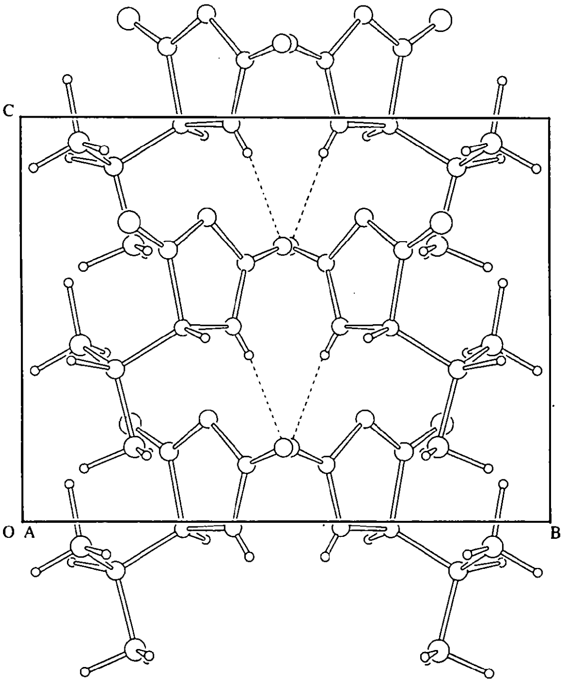

Fig. 2. Unit-cell contents of DL-valine NCA, projected onto the *bc* plane. Dashed lines indicate hydrogen bonds.

Experimental

Crystal data

$C_6H_9NO_3$
$M_r = 143.1$
Orthorhombic
$Pca2_1$
$a = 8.938$ (1) Å
$b = 10.207$ (2) Å
$c = 7.788$ (1) Å
$V = 710.6$ (2) Å^3
$Z = 4$
$D_x = 1.34$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 12 reflections
$\theta = 18$–$26°$
$\mu = 0.918$ mm^{-1}
$T = 293$ K
Needle
0.4 × 0.1 × 0.1 mm
Colourless

Data collection

AFC-4 diffractometer
ω–2θ scans
$T_{\min} = 0.938$, $T_{\max} = 0.986$
618 measured reflections
618 independent reflections
556 observed reflections
[$I > \sigma(F)$]

$\theta_{\max} = 62.5°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 8$
3 standard reflections
monitored every 50 reflections
intensity variation: 12%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.113$

$(\Delta/\sigma)_{\max} = -0.019$
$\Delta\rho_{\max} = 0.153$ e Å^{-3}
$\Delta\rho_{\min} = -0.237$ e Å^{-3}

$S = 1.084$
556 reflections
100 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.7440 (5)	0.4937 (3)	0.1819 (4)	0.059
O2	0.5597 (4)	0.3519 (3)	0.2563 (5)	0.057
O3	0.3726 (5)	0.2059 (5)	0.2438 (6)	0.082
N1	0.5898 (4)	0.3973 (4)	−0.0186 (5)	0.047
C1	0.6439 (6)	0.4232 (5)	0.1364 (6)	0.048
C2	0.4544 (6)	0.2779 (5)	0.1703 (8)	0.058
C3	0.4672 (5)	0.3030 (5)	−0.0201 (7)	0.047
C4	0.4995 (5)	0.1788 (6)	−0.1242 (8)	0.059
C5	0.6427 (6)	0.1100 (6)	−0.063 (1)	0.078
C6	0.5021 (6)	0.2104 (7)	−0.3145 (9)	0.079

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

O1—C1	1.202 (6)	N1—C3	1.458 (5)
O2—C2	1.380 (6)	C2—C3	1.509 (8)
O2—C1	1.403 (6)	C3—C4	1.533 (8)
O3—C2	1.185 (6)	C4—C6	1.517 (9)
N1—C1	1.327 (6)	C4—C5	1.536 (7)
C2—O2—C1	109.1 (4)	O2—C2—C3	109.4 (4)
C1—N1—C3	114.4 (4)	N1—C3—C2	99.3 (4)
O1—C1—N1	131.3 (5)	N1—C3—C4	114.1 (4)
O1—C1—O2	120.9 (5)	C2—C3—C4	113.2 (5)
N1—C1—O2	107.8 (4)	C6—C4—C3	110.1 (5)
O3—C2—O2	121.7 (6)	C6—C4—C5	112.8 (5)
O3—C2—C3	128.9 (6)	C3—C4—C5	111.8 (4)

Data collection: *AFC*-4 (Rigaku Corporation, 1974). Cell refinement: *RSLC*-3 (Sakurai, 1967). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: AS1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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7-Hydroxy-4-methylcoumarin Monohydrate

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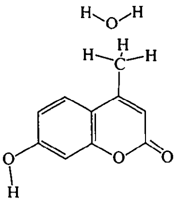
Abstract

The crystal structure of the title compound, $C_{10}H_8O_3.H_2O$, is stabilized by three intermolecular contacts of the O—H···O type involving the water molecules of crystallization. The coumarin moiety is planar and the hydroxy group is located in the plane of the benzene ring.

Comment

The title compound, (I), a hydroxycoumarin laser dye, has been used in laser gain studies (Masilamani & Sivaram, 1982). It is also known as Coumarin 4 (Eastman Kodak Company, Rochester, NY, USA) and Umbelliferon 47.



(I)

An *ORTEP* view (Johnson, 1976) of the title molecule with atomic labeling is shown in Fig. 1. Bond lengths and angles in the coumarin moiety are normal (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985; Murthy, Ramamurthy & Venkatesan, 1988). The coumarin moiety is planar [χ^2(pyrone ring) = 62.2 and O13—C7—C8—C9 = 178.9 (2)°].

The packing of the molecules in the unit cell viewed near the *a* axis is shown in Fig. 2. The molecules are linked by three hydrogen bonds of the O—H···O type to water molecules of crystallization, two of the interactions involving the carbonyl O atom [O2···O11$^{\rm i}$ 2.790 (2), O2—H2*A* 0.83 (3), H2*A*···O11$^{\rm i}$ 1.97 (3) Å and O2—H2*A*···O11$^{\rm i}$ 172.5 (1)°; O2···O11$^{\rm ii}$ 2.873 (2), O2—H2*B* 0.88 (3), H2*B*···O11$^{\rm ii}$ 2.00 (3) Å and O2—H2*B*···O11$^{\rm ii}$ 169.5 (1)°; symmetry code: (i) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (ii) $x-\frac{1}{2}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$] and one involving the hydroxy O atom [O13···O2$^{\rm iii}$ 2.655 (2), O13—H13 0.87 (2), H13···O2$^{\rm iii}$ 1.78 (2) Å and O13—H13···O2$^{\rm iii}$ 174.0 (1)°; symmetry code: (iii) $1-x$, $-y$, $1-z$].

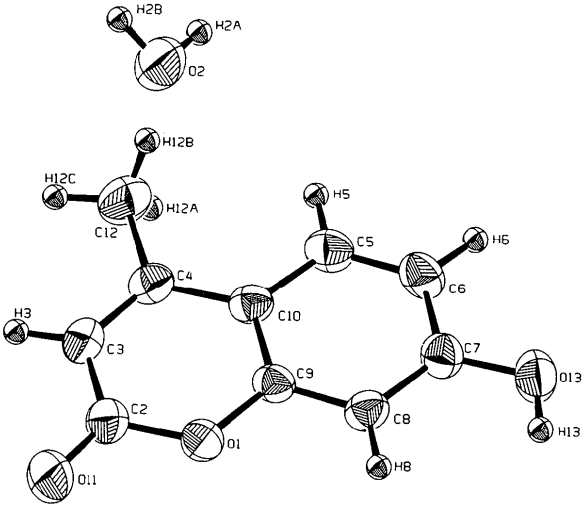


Fig. 1. *ORTEP* (Johnson, 1976) drawing (50% probability ellipsoids) of the title compound and the atomic numbering scheme.

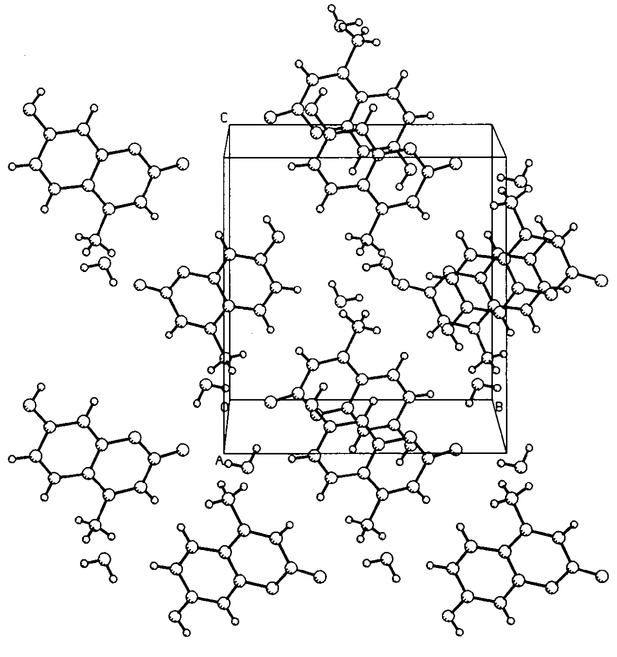


Fig. 2. Molecular packing of the title compound in the unit cell viewed close to the *a* axis.

Experimental

Crystals of the title compound (Exiton Chemical Company, Dayton, Ohio 45431, USA) were grown from acetonitrile by slow evaporation.