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N-Carboxy-L-aspartic anhydride benzyl ester

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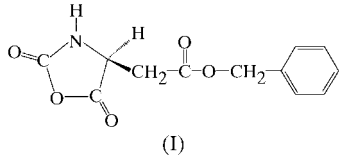
The structure of the title compound, benzyl (1,2,3,4-tetrahydro-2,5-dioxo-1,3-oxazol-4-yl)acetate, $C_{12}H_{11}NO_5$, has been determined in an attempt to explain the polymerization observed in the solid state. The molecules are linked by intermolecular hydrogen bonds between the imino group of the five-membered ring and an adjacent carbonyl O atom, along the *c* axis. Intramolecular hydrogen bonds are also formed, between the imino group and the carbonyl O atom of the ester group. The five-membered rings are arranged in a layer, sandwiched by layers incorporating the benzyl groups. This structure is thought to be preferable for the polymerization of the compound in the solid state, because the five-membered rings can react with each other in the layer.

Comment

N-Carboxy anhydrides (NCAs) of amino acids are crystalline compounds and are usually polymerized in solution to prepare polypeptides (Bamford *et al.*, 1956). Purified amino acid NCA crystals are sensitive to moisture and are polymerized or decomposed by water. When butylamine is added to amino acid NCA crystals immersed in a liquid such as hexane, decane, *etc*., which cannot dissolve the crystals, polymerization takes place in the solid state. The authors studied this solid-state polymerization and found that polymerizability is extremely dependent on the kind of amino acid NCA used.



(I)

The crystal structures of amino acid NCAs were not studied for a long time after an early report by Leuchs (1906). One of the present authors has reported the crystal structures of glycine NCA (Kanazawa *et al.*, 1976*a*) and L-alanine NCA (Kanazawa *et al.*, 1976*b*), and discussed their polymerizability with reference to the crystal structure (Kanazawa & Kawai, 1980). In addition, the crystal structures of Ag–benzyl-L-glutamate NCA (Kanazawa *et al.*, 1978*a*), L-leucine NCA (Kanazawa *et al.*, 1978*b*), L-valine NCA (Kanazawa *et al.*, 1984), DL-valine NCA (Takenaka *et al.*, 1994), DL-phenylalanine NCA (Kanazawa *et al.*, 1997) and L-phenylalanine NCA (Kanazawa, 2000) have been determined.

The polymerization of L-leucine NCA, which was the most reactive in the solid state among the NCAs studied, has been studied in detail (Kanazawa *et al.*, 1982; Kanazawa, 1992*a*,*b*). The reactivity of amino acid NCAs in the solid state is largely dependent on the purity of the crystals. The measurement of the molecular weight of the resulting polypeptides is very important in order to study the solid-state polymerization of amino acid NCAs in more detail. However, the usual polypeptides, such as poly(L-alanine), poly(L-valine) and poly(L-leucine), do not dissolve in the usual organic compounds, but do dissolve in strong acids, such as dichloroacetic acid and trifluoroacetic acid. On the other hand, polypeptides prepared by the polymerization of the NCAs of benzyl esters of such

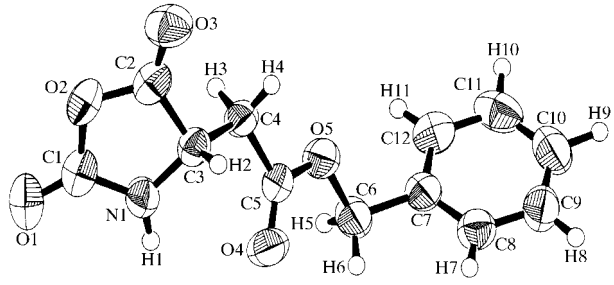


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the numbering of the atoms. H atoms are drawn as small circles of arbitrary radii.

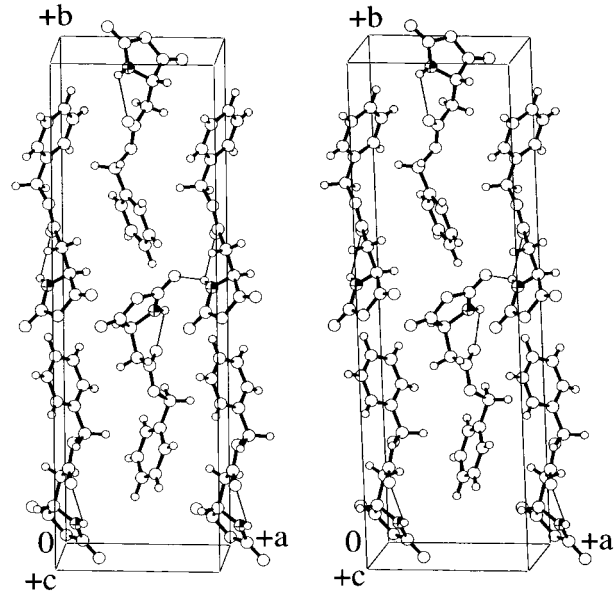


Figure 2
A stereopacking diagram for (I). The hydrogen bonds are indicated by thin solid lines.

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amino acids as glutamic or aspartic acids can be dissolved in common organic solvents, such as dioxane and *N*,*N*-dimethylformamide.

The polymerization of the title compound, (I), is much more reactive in the solid state than in solution; the polymer conversion in the solid-state polymerization of (I) initiated by butylamine was 18% after 2 h at 303 K, while the conversion of the polymerization in solution in acetonitrile was about 5% under similar conditions. Since the purified compound, (I) (BLA NCA), is very sensitive to moisture and crystallizes as very thin plates, many crystallization and data-collection attempts were carried out to determine its crystal structure. Here, we present the crystal and molecular structure of (I).

The molecular structure of (I) and the atom-numbering scheme are given in Fig. 1. In the structure of (I), intermolecular N1—H1···O1($\frac{3}{2} - x$, $1 - y$, $z - \frac{1}{2}$) hydrogen bonds are formed [N1···O1 = 2.922 (4) Å, H1···O1 = 2.11 (4) Å and N1—H1···O1 = 155 (3)°]. In addition, intramolecular N1—H1···O4 hydrogen bonds are formed [N1···O4 = 2.852 (3) Å, H1···O4 = 2.44 (2) Å and N1—H1···O4 = 109 (2)°].

From Fig. 2, it can be seen that the five-membered NCA rings in (I) are packed in a layer and the benzyl ester groups are packed in another layer; these two layers are aligned alternately. The resulting sandwich structure is one of the important requirements for high reactivity in the solid state (Kanazawa, 1992*a*, 1998). In the crystal of DL-phenylalanine NCA, the sandwich structure was composed of D and L molecules (Kanazawa *et al.*, 1997), and its crystal was also reactive in the solid state.

Experimental

The synthesis of β-benzyl-L-aspartate (BLA) was carried out by the reaction of L-aspartic acid with benzyl alcohol in the manner described previously by Kanazawa (1992*a*). The title compound was obtained by the reaction of BLA with trichloromethyl chloroformate or triphosgen in tetrahydrofuran, similar to the method used for the preparation of other NCAs (Kanazawa, 1992*a*). The reaction product, (I), was recrystallized from a mixture of ethyl acetate and hexane, avoiding contamination by moisture.

Crystal data

$C_{12}H_{11}NO_5$
M_r = 249.22
Orthorhombic, $P2_12_12_1$
a = 7.995 (3) Å
b = 26.611 (5) Å
c = 5.4348 (7) Å
V = 1156.3 (5) Å^3
Z = 4
D_x = 1.432 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 120 reflections
θ = 5.0–32.7°
μ = 0.11 mm^{-1}
T = 288.2 K
Plate, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Rigaku R-AXIS IV imaging plate area-detector diffractometer
ω scans
2319 measured reflections
2115 independent reflections
1128 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.053
θ_{max} = 31.4°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 38$
$l = 0 \rightarrow 7$

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.197 (4)	N1—C1	1.341 (4)
O2—C1	1.402 (4)	N1—C3	1.447 (4)
O2—C2	1.379 (4)	C2—C3	1.515 (4)
O3—C2	1.185 (4)	C3—C4	1.535 (4)
O4—C5	1.189 (4)	C4—C5	1.504 (4)
O5—C5	1.339 (4)	C6—C7	1.507 (5)
O5—C6	1.478 (4)		
C1—O2—C2	109.9 (2)	O2—C2—C3	107.9 (3)
C1—N1—C3	112.9 (3)	N1—C3—C2	101.1 (3)
O1—C1—N1	130.0 (4)		
O1—C1—O2—C2	177.6 (3)	O3—C2—O2—C1	−179.4 (3)
O1—C1—N1—C3	−176.3 (3)	O3—C2—C3—N1	−179.0 (3)
O2—C1—N1—C3	3.1 (4)	N1—C1—O2—C2	−1.9 (3)
O2—C2—C3—N1	1.6 (3)	C1—O2—C2—C3	0.1 (3)
O2—C2—C3—C4	122.9 (3)		

Refinement

Refinement on F^2
$R(F)$ = 0.054
$wR(F^2)$ = 0.076
S = 1.08
2113 reflections
209 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.00065|F_o|^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 0.052 (5)

All H atoms were located in geometrially calculated positions and refined isotropically; the C—H distances were in the range 0.86 (3)–1.08 (3) Å and the N—H distance was 0.87 (3) Å. As the absolute structure, which was known from the chirality of the starting materials, could not be determined reliably from the Flack (1983) parameter, the Friedel pairs were merged. Systematically absent reflections indicated the space group to be $P2_12_12_1$.

Data collection: *PROCESS* (Rigaku, 1996); cell refinement: *PROCESS*; data reduction: *TEXSAN* (Version 1.11; Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN* (Version 1.10; Molecular Structure Corporation & Rigaku, 1999); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* (Version 1.11).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1204). Services for accessing these data are described at the back of the journal.

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