

## N-Carboxy-L-phenylalanine anhydride

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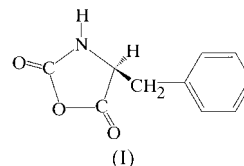
The molecules of the title compound, 4-benzyl-1,3-oxazolidene-2,5-dione,  $C_{10}H_9NO_3$ , are linked by intermolecular hydrogen bonds between the imino group of the five-membered ring and an adjacent carbonyl O-atom, along the  $c$  axis. The benzyl groups are stacked in a layer and the five-membered rings are arranged in another layer sandwiched by the benzyl group layer. This sandwich structure should explain the high polymerizability of the title compound in the solid state.

### Comment

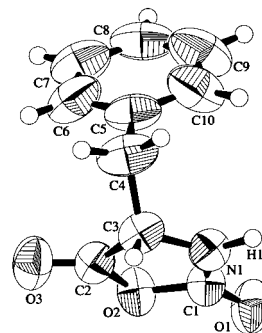
N-Carboxy anhydrides (NCAs) of amino acids are crystalline compounds and are usually polymerized in solution to prepare polypeptides (Bamford *et al.*, 1956). Several amino acid NCA crystals are known to be decomposed or polymerized by moisture. When butylamine is added to NCA crystals immersed in non-solvents, polymerization takes place in the solid state. The authors studied this solid-state polymerization and found the polymerizability of NCAs was extremely dependent on the kind of amino acid used. The crystal structures of amino acid NCAs were not studied for a long time after the very early report by Leuchs (1906).

The present author determined the crystal structures of glycine NCA (Kanazawa *et al.*, 1976a) and L-alanine NCA (Kanazawa *et al.*, 1976b) and discussed their polymerizability with reference to the crystal structure (Kanazawa & Kawai, 1980). In addition, the crystal structures of  $\gamma$ -benzyl-L-glutamate NCA (Kanazawa *et al.*, 1978a), L-leucine NCA (Kanazawa *et al.*, 1978b), L-valine NCA (Kanazawa & Ohashi, 1984), DL-valine NCA (Takenaka *et al.*, 1994) and DL-phenylalanine NCA (Kanazawa *et al.*, 1997) 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, 1992a,b). Recently, the title compound, (I), was found to be still more reactive than any other NCAs in the solid state, although it gave almost no reactivity in solution (Kanazawa, 1997). As compound (I) is very sensitive to moisture in air, it often polymerizes spontaneously in the crystallization process. Thus, crystals suitable for the present X-ray work were obtained after many

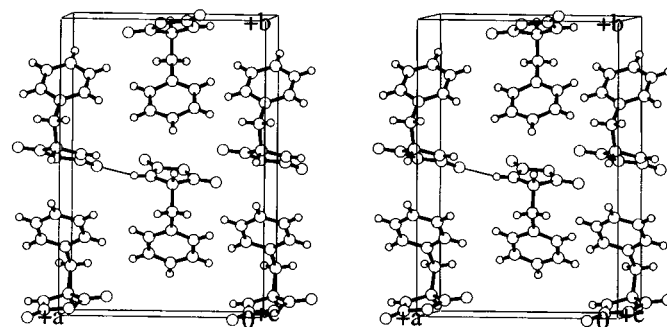
attempts. This paper describes the crystal structure of compound (I).



Intermolecular  $N1-H1 \cdots O1(\frac{1}{2} - x, -y, \frac{1}{2} + z)$  hydrogen bonds are formed along the  $c$  axis. Hydrogen-bond lengths and angles are  $N1 \cdots O1$  2.912 (2),  $H1 \cdots O1$  2.03 (2) Å and  $N1-H1 \cdots O1$  162 (2)°. From Fig. 2, it can be seen that the benzyl groups are in a layer and the benzene rings seem almost parallel to each other. The five-membered NCA rings are packed in another layer and these two layers are aligned alternately. The five-membered rings should easily react with one another within the layer. In fact, electron microscopy suggests that the polymerization mainly proceeds along the  $c$  axis. This sandwich structure is one of the preferred requirements for high reactivity in the solid state (Kanazawa, 1992a). In the crystal of DL-phenylalanine NCA, a sandwich structure composed of D and L molecules was observed (Kanazawa *et al.*, 1997), and the crystal was also reactive in the solid state.

**Figure 1**

The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme (ORTEP; Johnson, 1976). H atoms are drawn as small circles of arbitrary radii and only H1 is numbered.

**Figure 2**

Stereo packing diagram for (I). Note the hydrogen bond is indicated by a solid line.

Experimental

Compound (I) was obtained from L-phenylalanine by phosgenation in tetrahydrofuran with trichloromethyl chloroformate, using a method similar to that used for the other NCAs (Kanazawa & Kawai, 1980). The reaction product was purified by recrystallization from a solution in a mixture of ethyl acetate and hexane. Crystals for X-ray analysis were obtained from a solution in ethyl acetate with hexane vapour at about 283 K, avoiding contamination by moisture.

Crystal data

C<sub>10</sub>H<sub>9</sub>NO<sub>3</sub>  
*M<sub>r</sub>* = 191.19  
 Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 10.881 (2) Å  
*b* = 15.753 (2) Å  
*c* = 5.4764 (5) Å  
*V* = 938.7 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.353 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 1440 reflections  
 $\theta = 1.25\text{--}29.02^\circ$   
 $\mu = 0.101\text{ mm}^{-1}$   
*T* = 293.2 K  
 Needle, colourless  
 0.25 × 0.15 × 0.15 mm

Data collection

Rigaku R-AXIS IV IP  
 diffractometer  
 $\omega$  scans  
 6823 measured reflections  
 1427 independent reflections  
 1032 reflections with  $F^2 > 2\sigma(F^2)$

*R*<sub>int</sub> = 0.059  
 $\theta_{\text{max}} = 29.02^\circ$   
*h* = -14 → 14  
*k* = -21 → 21  
*l* = -7 → 7

Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.055  
*wR*(*F*<sup>2</sup>) = 0.158  
*S* = 1.250  
 1427 reflections  
 133 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/(\sigma^2(F_o^2) + \{0.067[\max(F_o^2, 0) + 2F_c^2]/3\}^2)$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.21\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.17\text{ e \AA}^{-3}$   
 Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic  
 Extinction coefficient: 0.075 (9)

Table 1

Selected geometric parameters (Å, °).

O1—C1	1.207 (3)	N1—C3	1.447 (4)
O2—C1	1.388 (3)	C2—C3	1.508 (4)
O2—C2	1.372 (3)	C3—C4	1.542 (4)
O3—C2	1.187 (4)	C4—C5	1.513 (4)
N1—C1	1.329 (3)		
C1—O2—C2	109.4 (2)	O2—C2—O3	122.3 (3)
C1—N1—C3	112.7 (2)	O2—C2—C3	108.4 (2)
O1—C1—O2	119.9 (2)	O3—C2—C3	129.3 (3)
O1—C1—N1	131.2 (3)	N1—C3—C2	100.6 (2)
O2—C1—N1	108.9 (2)		
O1—C1—O2—C2	179.7 (3)	O3—C2—C3—N1	-179.9 (3)
O1—C1—N1—C3	179.7 (3)	O3—C2—C3—C4	-56.7 (4)
O2—C1—N1—C3	1.2 (3)	C1—N1—C3—C2	-0.3 (3)
O2—C2—C3—N1	-0.7 (3)	C1—N1—C3—C4	-120.7 (3)
O3—C2—O2—C1	-179.3 (3)		

As the absolute structure could not be determined reliably from the Flack parameter and since it is known from the synthesis, the Friedel pairs were merged. Extinction conditions indicated that the space group is *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. H atoms were located at geometrically calculated positions and were fixed in refinement, except for H1 attached to N1, which was freely refined.

Data collection: *PROCESS* (Rigaku, 1996); cell refinement: *PROCESS*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1122). Services for accessing these data are described at the back of the journal.

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