

**(3*S*)-Benzyl *N*-(1-hydroxy-2,5-dioxo-  
 pyrrolidin-3-yl)carbamate: two-  
 dimensional sheets built from  
 $O-H \cdots O$ ,  $N-H \cdots O$ ,  $C=O \cdots C=O$   
 and  $C-H \cdots O$  interactions linked into a  
 three-dimensional complex framework  
 via  $C-H \cdots \pi(\text{arene})$  interactions**

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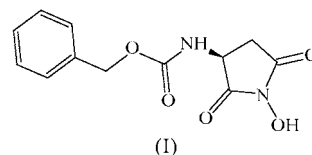
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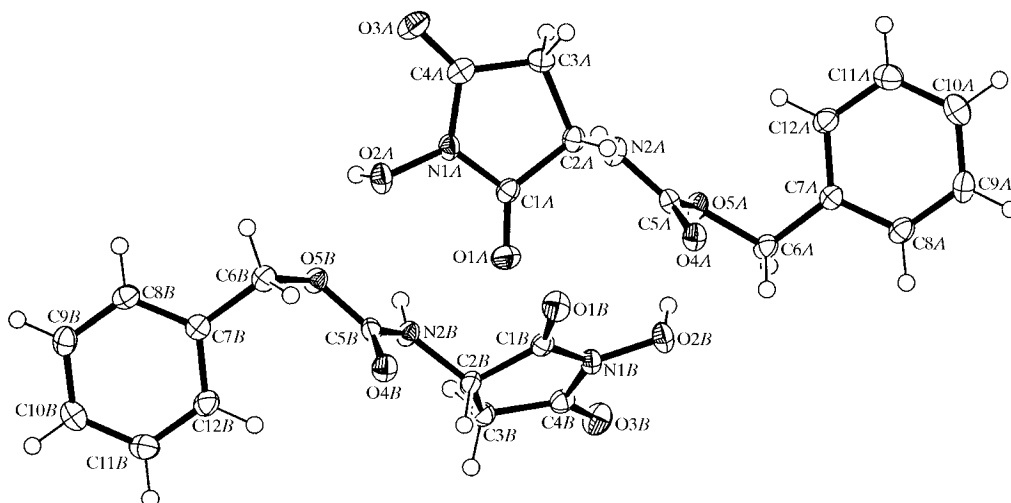
The title compound,  $C_{10}H_{12}O_5N_2$ , crystallizes with two independent molecules in the asymmetric unit. The molecules in the crystal structure are arranged into one-dimensional substructural ribbon motifs stabilized by a combination of two  $O-H \cdots O$  and three  $N-H \cdots O$  intermolecular hydrogen bonds, and also augmented by short  $C=O \cdots C=O$  carbonyl-carbonyl interactions. Two intermolecular  $C-H \cdots O$  short contacts between adjacent ribbons generate complex two-dimensional sheets on the *ab* plane. Adjacent sheets are linked via  $C-H \cdots \pi(\text{arene})$  interactions, resulting in a complex three-dimensional framework.

**Comment**

The title compound, (I), is a cyclic derivative of L-aspartic acid and belongs to the group of chiral *N*-hydroxysuccinimides. With the aim of synthesizing a new class of L-aspartic acid-based sulfonic esters of *N*-hydroxysuccinimides, we obtained (I) by reacting hydroxylamine with Cbz-L-aspartic acid anhydride (Cbz is carbobenzoxy) in a water-dioxane system. As part of our studies of *N*-oxysuccinimide ring geometry (Stefanowicz *et al.*, 2005, 2006), we report here the molecular and supramolecular structure of (I), which offers a wide range of intermolecular interactions, such as classical  $N-H \cdots O$  and  $O-H \cdots O$  hydrogen bonds, short carbonyl-carbonyl  $O \cdots C$  interactions, and  $C-H \cdots O$  and  $C-H \cdots \pi(\text{arene})$  contacts.



Compound (I) crystallizes in the space group  $P2_1$  with two independent molecules in the asymmetric unit, denoted *A* and *B* (Fig. 1). Superposition of these two molecules is shown in Fig. 2. They differ mainly in the orientation of the benzyl group, with the  $O5-C6-C7-C8$  torsion angles being  $166.6(2)$  and  $-117.6(2)^\circ$  for molecules *A* and *B*, respectively. Atoms N1 of molecules *A* and *B* are characterized by planar geometry, with deviations from the plane defined by atoms C1/C4/O2 of  $0.023(2)$  and  $0.019(2)$  Å, respectively. Comparison of these values with the data available for analogous compounds such as *N*-hydroxysuccinimide [ $0.061(2)$  Å; Jones, 2003] and *N*-hydroxyphthalimide [ $0.108(6)$  Å; Miao *et al.*, 1995] indicates increased  $sp^2$  character of the succinimide N atom for (I). The succinimide ring geometry of (I) is also slightly puckered compared with the virtually planar geometries of the *N*-hydroxyphthalimide and *N*-hydroxysuccinimide five-membered rings, which both have r.m.s. deviations of less than  $0.02$  Å. This difference can be explained by the substi-



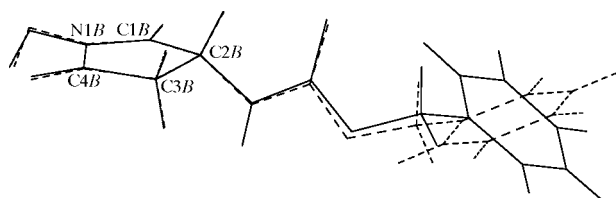
**Figure 1**

The two molecules of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

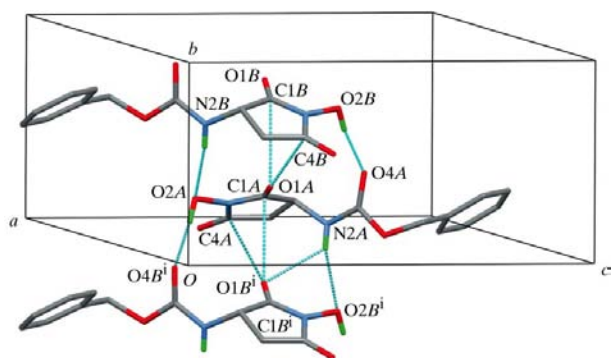
tution of atoms C2A/B by a benzyloxycarbonylamino group in (I), while in the other two compounds, both aromatic or methylene C atoms are geometrically equal. The puckering parameters (Cremer & Pople, 1975) for (I) are  $q_2 = 0.079$  (2) Å and  $\psi_2 = 227$  (1)° for molecule A, and  $q_2 = 0.081$  (2) Å and  $\psi_2 = 251$  (1)° for molecule B, indicating a twisted conformation on C1A—C2A and an approximate envelope conformation at C2B for the five-membered rings of molecules A and B, respectively.

The hydrogen-bond network is built up from the combination of three N—H···O and two O—H···O hydrogen bonds that link molecules A with neighbouring molecules B to form one-dimensional substructural ribbon motifs, augmented by short C=O···C=O carbonyl–carbonyl interactions between adjacent succinimide rings (Fig. 3). The strength of the C=O···C=O interactions can be compared with medium-strength hydrogen bonds (Allen *et al.*, 1998). Adjacent ribbons are linked *via* chains of C—H···O contacts between molecules of the same type to form two-dimensional sheets (Fig. 4). Only short C—H··· $\pi$ (arene) interactions link neighbouring sheets, generating a three-dimensional complex network (Fig. 5).

Atoms N2B and O2B from molecule B act as hydrogen-bond donors to atoms O2A and O4A from molecule A, respectively. The combination of these two hydrogen bonds gives an  $R_2^2(14)$  ring (Bernstein *et al.*, 1995). Atom O2A also acts as a hydrogen-bond donor to atom O4B of a neighbouring molecule at  $(x, y - 1, z)$ , and atom N2A is a hydrogen-bond



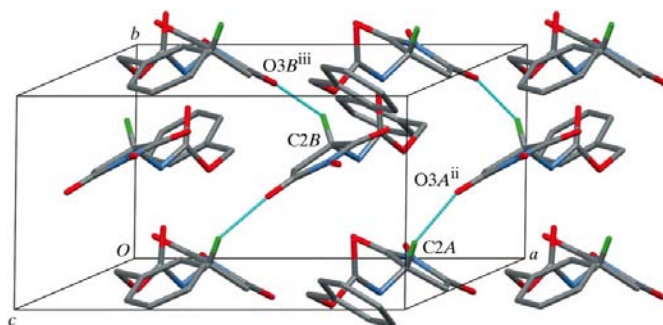
**Figure 2**  
The superposition of molecules A and B. The reference atoms are N1, C1, C2, C3 and C4.



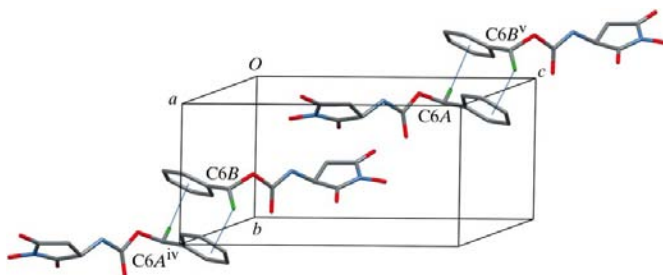
**Figure 3**  
A view showing the formation of ribbons of alternately linked A and B molecules, with one  $R_2^2(13)$ , two  $R_2^2(14)$  and one  $R_2^2(5)$  ring, along the [010] direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Dashed lines indicate the various intermolecular interactions. (The symmetry code is as in Table 1.)

donor to atoms O1B and O2B, both at  $(x, y - 1, z)$ , so  $R_2^2(13)$ ,  $R_2^2(14)$  and  $R_2^2(5)$  ring motifs are generated (Fig. 3). Propagation of these motifs by simple translation along the *b* axis gives a one-dimensional substructural ribbon motif, which is additionally supported by C=O···C=O interactions between adjacent A and B molecules, *e.g.* O1A···C1B [2.848 (2) Å] and O1A···C4B [3.074 (2) Å], and O1B<sup>i</sup>···C1A [3.028 (2) Å] and O1B<sup>i</sup>···C4A [2.938 (2) Å] (Fig. 3). These contacts do not occur in the crystal structures of *N*-hydroxyphthalimide (Miao *et al.*, 1995) and *N*-hydroxysuccinimide (Jones, 2003). Atoms C2A and C2B act as hydrogen-bond donors to atoms O3A<sup>ii</sup> and O3B<sup>iii</sup>, respectively, both linking molecules of the same type from adjacent ribbons (Fig. 4). Propagation of these short C—H···O contacts by a  $2_1$  screw axis  $(\frac{1}{2}, y, \frac{1}{2})$  and translation along the *a* axis generate a two-dimensional sheet of C—H···O chains linked into ribbons in the *ab* plane. Adjacent sheets are linked *via* C—H··· $\pi$ (arene) interactions, with C6A··· $\pi$ (arene)<sup>iv</sup> and C6B··· $\pi$ (arene)<sup>v</sup> distances of 3.401 (2) and 3.428 (2) Å, respectively, providing a complex three-dimensional framework (see Fig. 5 for symmetry codes).

It is worth mentioning that the characteristic C(5) motif of the O—H···O hydrogen-bonding combination in simple *N*-hydroxyimides (Miao *et al.*, 1995; Jones, 2003) is absent from the structure of (I). The hydrogen-bonding geometry is listed in Table 1.



**Figure 4**  
A view showing the formation of two-dimensional sheets in the *ab* plane *via* C—H···O interactions (dashed lines) linking molecules of one type along the [010] direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. (The symmetry codes are as in Table 1.)



**Figure 5**  
The C—H··· $\pi$ (arene) interactions (thin lines) between adjacent sheets of (I). For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry codes: (iv)  $x, 1 + y, -1 + z$ ; (v)  $x, -1 + y, 1 + z$ .]

Experimental

The synthesis of (3*S*)-benzyl *N*-(1-hydroxy-2,5-dioxopyrrolidin-3-yl)-carbamate was carried out according to the following procedure. Cbz-L-aspartic acid anhydride (1 g, 4 mmol) was added to a solution of hydroxylamine hydrochloride, NH<sub>3</sub>(OH)Cl (0.30 g, 4 mmol), and NaOH (0.16 g, 4 mmol) dissolved in a water–dioxane mixture (1:1 v/v; 4 ml). The solution was stirred for 15 min at room temperature and then for 1 h at 323 K. The water and dioxane were then evaporated under reduced pressure and the residue was heated at 398 K for 20 min *in vacuo*. The product was extracted with anhydrous ethyl acetate (30 ml). Single crystals of (I) were obtained by slow evaporation from an ethyl acetate solution (yield 77%; m.p. 413–414.5 K). The crystals of (I) are hygroscopic and not stable in air; on removal from the ethyl acetate solution they become matt and break. Analysis:  $[\alpha]_D^{24} = -39.7^\circ$  ( $c = 1.40$ , MeOH); ESI–MS  $m/z$ : 287  $[MNa]^+$ .

Crystal data

C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>  $V = 1188.8(8) \text{ \AA}^3$   
 $M_r = 264.24$   $Z = 4$   
 Monoclinic,  $P2_1$  Mo  $K\alpha$  radiation  
 $a = 12.910(3) \text{ \AA}$   $\mu = 0.12 \text{ mm}^{-1}$   
 $b = 7.077(4) \text{ \AA}$   $T = 100(2) \text{ K}$   
 $c = 14.001(3) \text{ \AA}$   $0.28 \times 0.25 \times 0.20 \text{ mm}$   
 $\beta = 111.67(3)^\circ$

Data collection

Oxford Diffraction KM-4 CCD 3640 independent reflections  
 area-detector diffractometer 3070 reflections with  $I > 2\sigma(I)$   
 17662 measured reflections  $R_{int} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$  H atoms treated by a mixture of  
 $wR(F^2) = 0.083$  independent and constrained  
 $S = 1.00$  refinement  
 3640 reflections  $\Delta\rho_{max} = 0.22 \text{ e \AA}^{-3}$   
 355 parameters  $\Delta\rho_{min} = -0.22 \text{ e \AA}^{-3}$

The absolute configuration of the chiral C atom was established in agreement with the absolute configuration of the L-enantiomer of aspartic acid, which was used for the synthesis of compound (I). Friedel opposites were merged for the refinement. Other investigations showed the lack of racemization in the synthetic route of the present compound (Stefanowicz *et al.*, 2006). Only the aliphatic and aromatic H atoms were positioned geometrically and refined as riding on their parent atoms, with C–H = 0.95–1.00 Å and  $U_{iso}(H) = 1.2U_{eq}(C)$ . Other H atoms were located in a difference Fourier

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2A–H1A $\cdots$ O4B <sup>i</sup>	0.87 (3)	1.80 (3)	2.667 (2)	173 (3)
N2A–H2NA $\cdots$ O2B <sup>i</sup>	0.84 (3)	2.39 (3)	3.184 (3)	158 (2)
N2A–H2NA $\cdots$ O1B <sup>i</sup>	0.84 (3)	2.47 (2)	3.000 (3)	122 (2)
O2B–H1B $\cdots$ O4A	0.80 (3)	1.90 (3)	2.689 (2)	172 (3)
N2B–H2NB $\cdots$ O2A	0.84 (3)	2.43 (3)	3.237 (3)	162 (2)
C2A–H2A $\cdots$ O3A <sup>ii</sup>	1.00	2.39	3.004 (3)	119
C2B–H2B $\cdots$ O3B <sup>iii</sup>	1.00	2.43	3.035 (3)	118

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

map and their positions refined freely, with N–H = 0.84 (3) Å and O–H = 0.80 (3)–0.87 (3) Å; their  $U_{iso}(H)$  values were constrained to  $1.2U_{eq}(\text{parent atom})$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3069). Services for accessing these data are described at the back of the journal.

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