Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

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

	x	y	z	U_{eq}
C(1)	0.1737 (4)	0.7740 (3)	0.22501 (14)	0.0260 (4)
N(2)	0.3005 (4)	0.6605 (2)	0.2426 (2)	0.0324 (5)
C(3)	0.2055 (4)	0.5950 (2)	0.3148 (2)	0.0245 (5)
N(4)	0.0195 (4)	0.6612 (2)	0.35282 (15)	0.0286 (4)
C(5)	−0.0284 (3)	0.7733 (3)	0.30110 (14)	0.0242 (4)
N(6)	0.0160 (4)	0.8859 (2)	0.3521 (2)	0.0293 (5)
C(7)	0.2074 (4)	0.9502 (2)	0.3173 (2)	0.0256 (5)
N(8)	0.3093 (4)	0.8848 (2)	0.24709 (15)	0.0305 (5)
C(9)	−0.1483 (5)	0.6094 (3)	0.4193 (2)	0.0311 (6)
C(10)	−0.1487 (5)	0.9343 (3)	0.4213 (2)	0.0319 (6)
O(11)	0.2733 (3)	0.4921 (2)	0.34124 (13)	0.0316 (4)
O(12)	0.2778 (3)	1.0523 (2)	0.34529 (14)	0.0334 (4)
O(1*W*)	0.2632 (8)	0.7981 (3)	0.0018 (2)	0.097 (2)

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

C(1)—N(2)	1.435 (4)	N(4)—C(5)	1.448 (3)
C(1)—N(8)	1.449 (3)	C(5)—N(6)	1.443 (3)
C(1)—C(5)	1.560 (3)	N(6)—C(7)	1.359 (3)
N(2)—C(3)	1.362 (3)	N(6)—C(10)	1.445 (3)
C(3)—O(11)	1.235 (3)	C(7)—O(12)	1.238 (3)
C(3)—N(4)	1.364 (3)	C(7)—N(8)	1.355 (3)
N(4)—C(9)	1.442 (3)		
N(2)—C(1)—N(8)	114.8 (2)	N(6)—C(5)—N(4)	114.6 (2)
N(2)—C(1)—C(5)	102.7 (2)	N(6)—C(5)—C(1)	103.4 (2)
N(8)—C(1)—C(5)	102.6 (2)	N(4)—C(5)—C(1)	103.5 (2)
C(3)—N(2)—C(1)	113.1 (2)	C(7)—N(6)—C(5)	112.2 (2)
O(11)—C(3)—N(2)	126.0 (2)	C(7)—N(6)—C(10)	123.7 (2)
O(11)—C(3)—N(4)	125.3 (2)	C(5)—N(6)—C(10)	123.3 (2)
N(2)—C(3)—N(4)	108.6 (2)	O(12)—C(7)—N(8)	125.4 (2)
C(3)—N(4)—C(9)	122.8 (2)	O(12)—C(7)—N(6)	125.5 (2)
C(3)—N(4)—C(5)	111.9 (2)	N(8)—C(7)—N(6)	109.1 (2)
C(9)—N(4)—C(5)	123.3 (2)	C(7)—N(8)—C(1)	112.5 (2)

Refinement was on F^2 for all reflections except for three low-angle reflections flagged for potential systematic errors.

All H atoms were located in the difference Fourier map. However, the H atoms of the water molecule were included in the refinement only in the riding-model approximation. Symmetry equivalents were measured for only several hundred high-order and, therefore, weak reflections, which account for the high value of R_{int}.

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of the Structure of *N*-Carbamyl-D,L-aspartic Acid

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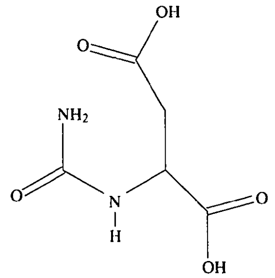
Abstract

The structure of the free acid form of *N*-carbamyl-D,L-aspartate, $C_5H_8N_2O_5$, has been redetermined. There are substantial differences between the conformation of the free acid form and the deprotonated form of *N*-carbamyl-L-aspartate. Detailed comparison with the structure of L-dihydroorotate shows that cyclization of *N*-carbamyl-L-aspartate results in only two significant changes in bond lengths and does not cause substantial stress.

Comment

The enzyme dihydroorotase catalyses the conversion of *N*-carbamyl-L-aspartate to L-dihydroorotate, which is the third reaction of the *denovo* pathway for pyrimidine nucleotide biosynthesis (Christopherson & Jones, 1980). It has been shown that the active site of this enzyme contains a Zn atom (Christopherson & Jones, 1980) and we have been studying zinc complexes of natural substrates and inhibitors of dihydroorotase. Crystals of *N*-carbamyl-D,L-aspartic acid were obtained as a byproduct of an attempt to grow crystals of a zinc complex of *N*-carbamyl-D,L-aspartate. The structures of this acid form of *N*-carbamyl-D,L-aspartate (Jagannatha Rao, Krishna Murthy, Appaji Rao & Vijayan, 1982) and of the dicyclohexylammonium salt of *N*-carbamyl-

L-aspartate (Zanotti, Monaco & Foote, 1984) have been reported previously. Both of these determinations were relatively imprecise ($R = 0.095$ and 0.10, respectively) and therefore detailed comparison of bond lengths with those in the present structure is inappropriate. There is a significant difference in the conformations of the free acid and deprotonated forms. In the acid form the carboxylate groups are *cis* [64.4 (1)°] with respect to one another and in the anionic form they are *trans* (174°). Conversely, in the acid form carboxylate group 1 [C(1),O(1),O(2)] is *trans* [166.9 (1)°] to the carbonyl group and in the anionic form it is *cis* (−62°). In all other respects the conformations are similar so the difference is best described as a rotation by approximately 60° about the C(2)—C(3) bond.



There are a number of strong intermolecular hydrogen bonds involving the carboxylate and amine groups. There is also a close intramolecular contact between O(2) and N(1)—HN(1) [2.644 (2) and 2.26 (2) Å]. It is unlikely that this interaction is a hydrogen bond, but it is an attractive interaction and probably stabilizes the near zero O(2)—C(1)—C(2)—N(1) torsion angle [4.5 (2)°].

As part of a study of the natural substrates and inhibitors of the enzyme dihydroorotase we have recently reported the structure of the methyl ester of L-dihydroorotate (Hambley, Phillips, Poiner & Christopherson, 1993). Since dihydrorotase converts *N*-carbamyl-L-aspartate to L-dihydroorotate, it is of interest to compare in detail bond lengths and angles in these two compounds. Cyclization is achieved by the formation of a bond between N(2) and C(4) with the elimination of a water molecule. Only two of the existing bonds are significantly altered by this cyclization; C(5)—N(2) lengthens from 1.340 (2) to 1.375 (7) Å and C(5)—O(5) shortens from 1.257 (2) to 1.233 (6) Å. The changes correspond to movement of electron density from N(2) away from the bond with C(5) and into the newly formed bond, and a concomitant increase in the electron density of the C(5)—O(5) bond. The largest change in the intra-ring angles is 2.3°; the angle at N(1) decreases by 1.9° and that at C(3) increases by 2.3° on ring closure. Thus, it appears that little stress arises from ring closure.

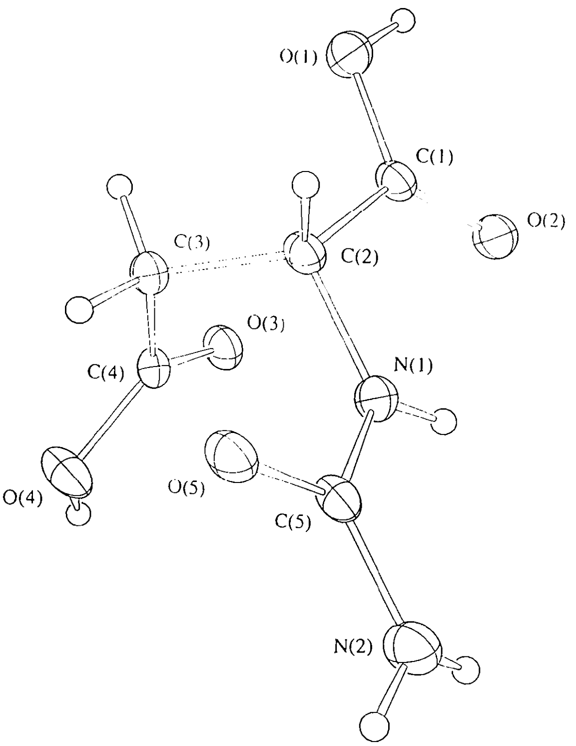


Fig. 1. *ORTEP* (Johnson, 1965) plot of *N*-carbamyl-D,L-aspartic acid, showing atomic labels (30% displacement ellipsoids).

Experimental

N-Carbamyl-DL-aspartic acid (2.85×10^{-4} mol) was dissolved in 8 ml of water and was added to a suspension of zinc hydroxide hydrate (1.40×10^{-4} mol) made up in 8 ml of water. Crystals were grown by slow evaporation of this solution.

Crystal data

$C_5H_8N_2O_5$
$M_r = 176.13$
Triclinic
$P\bar{1}$
$a = 6.443$ (2) Å
$b = 7.476$ (2) Å
$c = 8.058$ (3) Å
$\alpha = 72.27$ (2)°
$\beta = 80.82$ (3)°
$\gamma = 76.23$ (2)°
$V = 357.5$ (1) Å^3
$Z = 2$

$D_x = 1.635$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–12°
$\mu = 1.40$ mm^{-1}
$T = 294$ K
Triangular plate
0.12 × 0.11 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1348 measured reflections
1212 independent reflections
1141 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 25°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity variation: <1%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.043$
$S = 4.88$
1141 reflections
142 parameters
All H-atom parameters refined

$w = 4.62/[\sigma^2(F_o) + 0.00018F_o^2]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

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

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
C(1)	0.3036 (2)	0.3502 (2)	0.2914 (2)	1.97 (5)
C(2)	0.3155 (2)	0.5610 (2)	0.2333 (2)	1.96 (5)
C(3)	0.1632 (2)	0.6782 (2)	0.0922 (2)	2.19 (5)
C(4)	−0.0667 (2)	0.6786 (2)	0.1626 (2)	2.02 (5)
C(5)	0.3043 (2)	0.7979 (2)	0.3887 (2)	1.93 (5)
O(1)	0.3615 (2)	0.2707 (2)	0.1624 (1)	2.96 (5)
O(2)	0.2490 (2)	0.2673 (1)	0.4401 (1)	2.67 (5)
O(3)	−0.1363 (2)	0.5334 (1)	0.2339 (1)	2.59 (5)
O(4)	−0.1865 (2)	0.8513 (2)	0.1405 (2)	3.21 (5)
O(5)	0.3954 (2)	0.9005 (1)	0.2571 (1)	2.35 (5)
N(1)	0.2684 (2)	0.6299 (2)	0.3871 (2)	2.19 (5)
N(2)	0.2402 (2)	0.8508 (2)	0.5364 (2)	2.75 (5)
HO(1)	0.360 (3)	0.146 (3)	0.201 (3)	6 (1)
HO(4)	−0.315 (3)	0.841 (3)	0.184 (3)	5 (1)

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

C(2)—C(1)	1.518 (2)	O(1)—C(1)	1.312 (2)
O(2)—C(1)	1.208 (2)	C(3)—C(2)	1.537 (2)
N(1)—C(2)	1.446 (2)	C(4)—C(3)	1.499 (2)
O(3)—C(4)	1.217 (2)	O(4)—C(4)	1.313 (2)
O(5)—C(5)	1.257 (2)	N(1)—C(5)	1.334 (2)
N(2)—C(5)	1.340 (2)		
O(1)—C(1)—C(2)	112.0 (1)	O(2)—C(1)—C(2)	123.2 (1)
O(2)—C(1)—O(1)	124.8 (1)	C(3)—C(2)—C(1)	112.1 (1)
N(1)—C(2)—C(1)	107.6 (1)	N(1)—C(2)—C(3)	111.9 (1)
C(4)—C(3)—C(2)	111.2 (1)	O(3)—C(4)—C(3)	123.5 (1)
O(4)—C(4)—C(3)	113.5 (1)	O(4)—C(4)—O(3)	123.0 (1)
N(1)—C(5)—O(5)	121.0 (1)	N(2)—C(5)—O(5)	121.9 (1)
N(2)—C(5)—N(1)	117.1 (1)	C(5)—N(1)—C(2)	123.1 (1)

Lorentz and polarization corrections were applied using the *SDP* system (Frenz, 1985). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Refinement was performed by full-matrix least-squares methods using *SHELX*76 (Sheldrick, 1976). Non-H atoms were refined anisotropically and H atoms were located in the difference maps and refined isotropically. Graphics were obtained using *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and non-bonded interactions have been deposited with the IUCr (Reference: OH1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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30-Dechloro-30-methoxy-25-*O*-methyl-*N*-methylnaphthomycin A

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Abstract

The reaction of naphthomycin A with methyl iodide gives the title compound as the major product.

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