Structure of N^2-Carbamoyl-L-asparagine

By H. P. Yennawar and M. A. Viswamitra

*Department of Physics and ICMR Centre on Genetics and Cell Biology, Indian Institute of Science,
Bangalore 560 012, India*

Abstract. $C_5H_9N_3O_4$, $M_r = 175.1$, orthorhombic, $P2_12_12_1$, $a = 7.486$ (1), $b = 9.919$ (2), $c = 20.279$ (2) Å, $V = 1505.8$ Å³, $Z = 8$, $D_x = 1.54$, $D_m = 1.60$ Mg m⁻³, $\lambda(Cu\,K\alpha) = 1.5418$ Å, $\mu = 1.11$ mm⁻¹, $F(000) = 736$, $T = 300$ K, final $R = 0.032$ for 1345 observed reflections. The two independent molecules in the asymmetric unit are related by a pseudo twofold axis, with the asparagine side chains having different conformations [χ^2 being -132.1 (3) and 139.6 (2)°]. The crystal structure is stabilized by extensive hydrogen bonding, with a specific interaction between the carboxyl group of one molecule and the carbamoyl group of another forming hydrogen-bonded chains.

Introduction. N^2-Carbamoyl-L-asparagine is a modified amino acid. The structure was solved as part of our programme to study the interaction between modified amino acids and nucleic acid fragments.

Experimental. Crystals were grown from an aqueous solution of the compound (Sigma Chemicals) by direct evaporation. The density was measured by flotation in acetone/bromoform. Preliminary examination was performed by rotation and Weissenberg photography. Cell parameters were refined by least-squares calculations from 25 reflections with $4.3 \le \theta \le 42.2°$ on an Enraf–Nonius CAD-4 diffractometer. Intensity data from a crystal of dimensions $0.5 \times 0.2 \times 0.2$ mm were collected up to $(\sin\theta)/\lambda = 0.626$ Å⁻¹ with an ω–2θ scan using Ni-filtered Cu $K\alpha$ radiation. Two strong reflections ($11\bar{3}$, $\bar{1}1\bar{3}$) monitored periodically during data collection showed that the crystal was stable to X-rays. Index ranges of unique data were $0 \le h \le 9$, $0 \le k \le 12$, $0 \le l \le 25$. 1720 reflections were collected of which 1345 unique reflections were considered observed [$I > 3\sigma(I)$]. Structure solved by direct methods using *MULTAN*80 (Main *et al.*, 980). All the H atoms were located from difference Fourier maps. Full-matrix least-squares refinement with non-H atoms refined anisotropically and H atoms isotropically converged at $R = 0.032$ and $wR = 0.030$. S (goodness of fit) = 0.728. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. Maximum shift/e.s.d. ratio for non-H atoms = 0.02. Residual electron density in the

Table 1. *Final positional and equivalent isotropic thermal parameters of non-H atoms with e.s.d.'s given in parentheses*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	$B_{eq}(\text{Å}^2)$
Molecule A				
O(1)	0.3515 (2)	0.9980 (2)	−0.2171 (1)	2.99 (5)
O(2)	0.4263 (3)	1.1961 (2)	−0.2635 (1)	3.31 (5)
O(3)	0.4637 (3)	1.1918 (2)	−0.1081 (1)	3.98 (6)
O(4)	1.0186 (3)	1.0444 (2)	−0.2333 (1)	3.21 (5)
N(1)	1.0407 (3)	1.2608 (3)	−0.2636 (1)	3.29 (7)
N(2)	0.7698 (3)	1.1722 (3)	−0.2317 (1)	2.71 (6)
N(3)	0.7139 (4)	1.1779 (3)	−0.0469 (1)	4.13 (8)
C(1)	0.4651 (4)	1.0951 (3)	−0.2332 (1)	2.53 (6)
C(2)	0.6568 (4)	1.0597 (3)	−0.2129 (1)	2.37 (6)
C(3)	0.9461 (4)	1.1562 (3)	−0.2425 (1)	2.47 (6)
C(4)	0.6741 (4)	1.0234 (3)	−0.1401 (2)	2.73 (7)
C(5)	0.6100 (4)	1.1398 (3)	−0.0969 (2)	2.94 (7)
Molecule B				
O(5)	1.3219 (3)	0.8465 (2)	0.0889 (1)	3.56 (5)
O(6)	1.2502 (3)	1.0476 (2)	0.1309 (1)	3.29 (5)
O(7)	1.0878 (3)	1.0806 (2)	−0.0296 (1)	3.76 (6)
O(8)	0.6557 (2)	0.8928 (2)	0.1019 (1)	2.86 (5)
N(4)	0.6349 (3)	1.1199 (3)	0.1146 (1)	3.51 (7)
N(5)	0.9057 (3)	1.0198 (3)	0.0992 (1)	2.68 (6)
N(6)	1.1997 (4)	0.9032 (3)	−0.0835 (1)	3.98 (7)
C(6)	1.2098 (3)	0.9437 (3)	0.1044 (1)	2.39 (6)
C(7)	1.0195 (4)	0.9061 (3)	0.0841 (1)	2.35 (6)
C(8)	0.7281 (3)	1.0062 (4)	0.1053 (1)	2.29 (6)
C(9)	1.0126 (4)	0.8616 (3)	0.0114 (1)	2.47 (7)
C(10)	1.1036 (4)	0.9579 (3)	−0.0352 (1)	2.55 (7)

final difference Fourier map is within 0.203 and -0.152 e Å⁻³. The atomic scattering factors were those given by Cromer & Waber (1965) and all calculations were performed using the Enraf–Nonius (1981) *SDP* on a PDP 11/44 computer.

Discussion. The final positional and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.* Geometric data are listed in Table 2. The two molecules in the asymmetric unit, related by a pseudo twofold axis, are shown in Fig. 1. The

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44597 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular geometry; e.s.d.'s are in parentheses*

(*a*) Bond lengths (Å)

Molecule *A*		Molecule *B*	
O(1)–C(1)	1·326 (4)	O(5)–C(6)	1·317 (4)
O(3)–C(5)	1·232 (4)	O(7)–C(10)	1·229 (4)
O(2)–C(1)	1·211 (4)	O(6)–C(6)	1·202 (4)
N(2)–C(2)	1·452 (4)	N(5)–C(7)	1·447 (4)
N(2)–C(3)	1·348 (4)	N(5)–C(8)	1·342 (4)
O(4)–C(3)	1·249 (4)	O(8)–C(8)	1·251 (4)
C(4)–C(5)	1·528 (5)	C(9)–C(10)	1·507 (4)
C(1)–C(2)	1·534 (4)	C(6)–C(7)	1·530 (4)
N(3)–C(5)	1·333 (4)	N(6)–C(10)	1·331 (4)
N(1)–C(3)	1·327 (4)	N(4)–C(8)	1·340 (4)
C(2)–C(4)	1·525 (4)	C(9)–C(7)	1·540 (4)

(*b*) Valence angles (°)

Molecule *A*		Molecule *B*	
C(2)–N(2)–C(3)	121·5 (3)	C(8)–N(5)–C(7)	121·6 (3)
O(1)–C(1)–C(2)	111·6 (3)	O(5)–C(6)–C(7)	110·6 (3)
O(1)–C(1)–O(2)	124·9 (3)	O(5)–C(6)–O(6)	125·1 (3)
N(2)–C(2)–C(1)	107·4 (2)	N(5)–C(7)–C(6)	107·5 (2)
N(2)–C(2)–C(4)	112·7 (2)	N(5)–C(7)–C(9)	114·0 (2)
C(1)–C(2)–C(4)	113·1 (2)	C(6)–C(7)–C(9)	111·0 (2)
O(2)–C(1)–C(2)	123·4 (3)	O(6)–C(6)–C(7)	124·3 (3)
C(2)–C(4)–C(5)	110·6 (3)	C(7)–C(9)–C(10)	113·8 (3)
O(3)–C(5)–N(3)	122·8 (3)	O(7)–C(10)–N(6)	121·7 (3)
O(3)–C(5)–C(4)	119·3 (3)	O(7)–C(10)–C(9)	121·8 (3)
O(4)–C(3)–N(2)	120·5 (3)	O(8)–C(8)–N(5)	121·0 (3)
O(4)–C(3)–N(1)	120·7 (3)	O(8)–C(8)–N(4)	122·6 (2)
N(3)–C(5)–C(4)	117·9 (3)	N(6)–C(10)–C(9)	116·5 (3)
N(1)–C(3)–N(2)	118·9 (3)	N(5)–C(8)–N(4)	116·4 (3)

(*c*) Torsional angles (°)

Molecule *A*		Molecule *B*	
C(3)–N(2)–C(2)–C(1)	−156·1 (2)	C(8)–N(5)–C(7)–C(6)	−160·3 (2)
C(3)–N(2)–C(2)–C(4)	78·3 (3)	C(8)–N(5)–C(7)–C(9)	75·9 (4)
C(2)–N(2)–C(3)–O(4)	−3·2 (5)	C(7)–N(5)–C(8)–O(8)	4·7 (5)
C(2)–N(2)–C(3)–N(1)	175·8 (3)	C(7)–N(5)–C(8)–N(4)	−175·3 (3)
N(2)–C(2)–C(1)–O(2)	4·6 (4)	N(5)–C(7)–C(6)–O(6)	3·1 (4)
N(2)–C(2)–C(1)–O(1)	−179·2 (2)	N(5)–C(7)–C(6)–O(5)	−177·0 (2)
C(4)–C(2)–C(1)–O(1)	−53·9 (3)	C(9)–C(7)–C(6)–O(5)	−51·7 (3)
C(4)–C(2)–C(1)–O(2)	129·5 (3)	C(9)–C(7)–C(6)–O(6)	128·5 (3)
C(1)–C(2)–C(4)–C(5)	−58·5 (3)	C(6)–C(7)–C(9)–C(10)	−49·6 (4)
N(2)–C(2)–C(4)–C(5)	63·6 (3)	N(5)–C(7)–C(9)–C(10)	71·9 (3)
C(2)–C(4)–C(5)–O(3)	49·9 (3)	C(7)–C(9)–C(10)–O(7)	−41·4 (3)
C(2)–C(4)–C(5)–N(3)	−132·1 (3)	C(7)–C(9)–C(10)–N(6)	139·6 (2)

(*d*) Hydrogen-bond parameters

$X \cdots H–Y$	$X \cdots Y$	$H \cdots X$	$X \cdots H–Y$
O(1)–H17···O(4^ii)	2·56 (1) Å	1·6 (1) Å	167·6°
O(1)···H3–N(6^ii)	3·08 (1)	2·3 (1)	146·5
O(2)···H5–N(1^ii)	2·95 (1)	2·0 (1)	165·7
O(8)···H18–O(5^ii)	2·55 (1)	1·6 (1)	163·9
O(8)···H4–N(6^iii)	2·98 (1)	2·2 (1)	174·7
O(7)···H8–N(3^i)	2·98 (1)	2·2 (1)	169·2
O(7)···H9–N(3^v)	3·01 (1)	1·8 (1)	163·1
O(6)···H10–N(4^vi)	2·98 (1)	2·0 (1)	165·6
O(3)···H16–N(5^vii)	2·90 (1)	2·0 (1)	156·0
O(3)···H1–N(4^vii)	3·09 (1)	2·4 (1)	142·0

Symmetry code: (i) x, y, z; (ii) $x-1, y, z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, -z$; (iv) $2-x$, $y-\frac{1}{2}, -\frac{1}{2}-z$; (v) $x+\frac{1}{2}, \frac{5}{2}-y, -z$; (vi) $x+1, y, z$; (vii) $x-\frac{1}{2}, \frac{5}{2}-y, -z$.

asparagine side chains violate the twofold arrangement, the torsion angle χ^2 (IUPAC–IUB Commission on Biochemical Nomenclature, 1970), which defines the conformation about the C^α–C^β bond, being different in the two molecules [C(2)–C(4)–C(5)–N(3) = −132·1 (3)° and C(7)–C(9)–C(10)–N(6) = 139·6 (2)°]. The torsion angle χ^i (N–C^α–C^β–C^ν) is 63·6 (3)° in molecule *A* and 71·9 (3)° in molecule *B*. Thus the conformation of the side chain in both
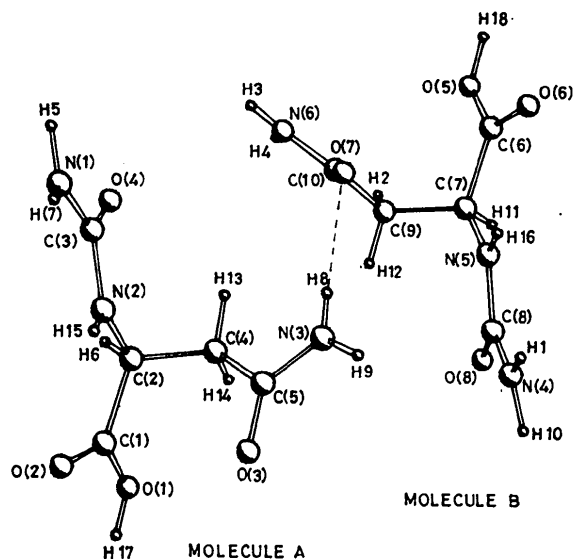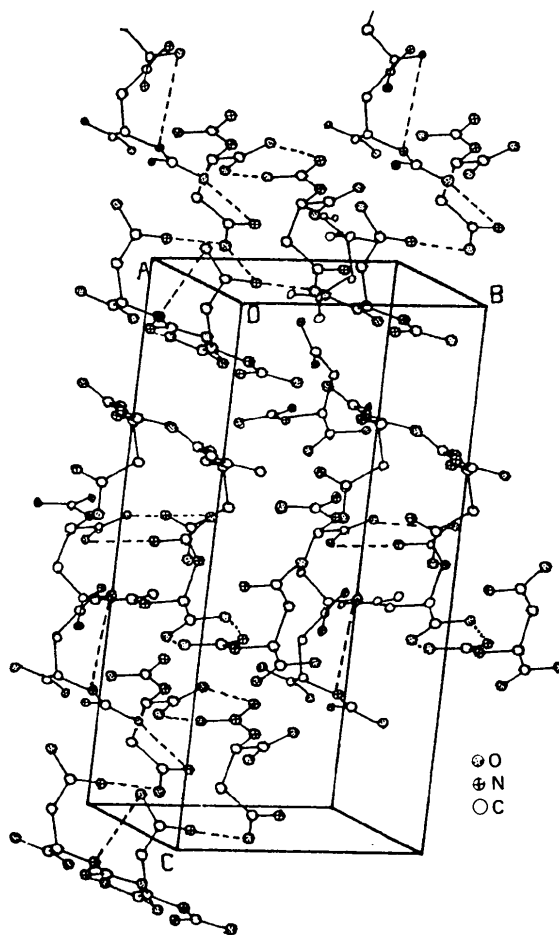

Fig. 1. View along **b** of the two independent molecules in the asymmetric unit.

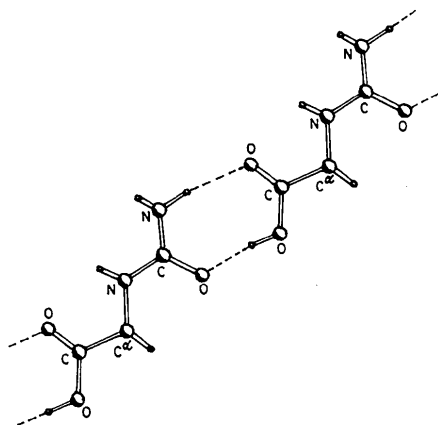Fig. 2. Unit-cell contents in minimum-overlap view.

Fig. 3. Specific interaction between the carboxyl group and the carbamoyl group. The asparagine side chains are not shown for clarity.

molecules corresponds to that which is sterically least favoured on the basis of population distribution studies (Bhat, Sasisekharan & Vijayan, 1979). The peptide link is essentially planar [$\omega = -179 \cdot 2$ (2)° (molecule A) and $-177 \cdot 0$ (2)° (molecule B)] and the N—C$^\alpha$ bond has a partial double-bond character as in other peptide units.

The crystal structure is stabilized by extensive hydrogen bonding (Table 2, Fig. 2). The hydrogen bonds involving the ureido O atoms O(4) and O(8) are strong [O(1)···O(4) = $2 \cdot 56$ Å and O(8)···O(5) = $2 \cdot 55$ Å] as found in the crystal structure of N-carbamoyl-L-aspartic acid (Jagannatha Rao, Krishna Murthy, Appaji Rao & Vijayan, 1982). Normally

O···O hydrogen-bond distances in organic crystals are of the order of $2 \cdot 72$ Å (Kuleshova & Zorkii, 1981). Atoms O(3) and O(7) of the asparagine side chain accept two hydrogen bonds each. According to Kuleshova & Zorkii (1981), only 31 such cases (with a common acceptor for two hydrogen bonds) were observed among 2220 hydrogen bonds in organic homomolecular crystals examined by them. The terminal O and N atoms of the carbamoyl group are connected to the carboxyl group of a neighbouring molecule through a pair of nearly parallel hydrogen bonds in a head-to-tail fashion (Fig. 3).

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Structure of 1-Methylsilatranone, CH₃Si(OCOCH₂)(OCH₂CH₂)₂N

BY VILMOS FÜLÖP AND ALAJOS KÁLMÁN*

Central Research Institute of Chemistry, Hungarian Academy of Science, Budapest, PO Box 17, H-1525 Hungary

AND PÁL HENCSEI, GÁBOR CSONKA AND ILONA KOVÁCS

Institute of Inorganic Chemistry, Technical University, Budapest, H-1521 Hungary

Abstract. 1-Methyl-2,8,9-trioxa-5-aza-1-silatricyclo-[3.3.3.0^{1,5}]undecan-3-one, $C_7H_{13}NO_4Si$, $M_r = 203 \cdot 27$, monoclinic, $P2_1/c$, $a = 8 \cdot 348$ (1), $b = 10 \cdot 931$ (1), $c = 9 \cdot 890$ (1) Å, $\beta = 91 \cdot 95$ (1)°, $V = 902 \cdot 0$ (3) Å^3, $Z = 4$, $D_x = 1 \cdot 50$ Mg m^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1 \cdot 5418$ Å, $\mu = 2 \cdot 21$ mm^{-1}, $F(000) = 432$, $T = 295$ (1) K, final $R = 0 \cdot 040$ for 1679 unique observed reflections. The structure of the title compound is compared with those of the analogous silatranes and silatranones bearing various substituents [p-F–C₆H₄–, m-CF₃–C₆H₄–,

* To whom correspondence should be addressed.