The intensity data were collected at variable scan rates from 4 to 29.3° min^{-1} depending on intensity. Stationary backgrounds were measured on both sides of a peak, each for one-half of the scan time. The structure was solved by direct methods and difference Fourier techniques, and refined by blocked-cascade least-squares refinement (Sparks, 1961). Non-H atoms were refined with anisotropic and H atoms with isotropic displacement parameters. Calculations were performed on the Data General micro-eclipse computer. Software used for structure solution, refinement and molecular graphics: *SHELXTL* (Sheldrick, 1985).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Acetyl-L-phenylalanyl-L-alaninamide

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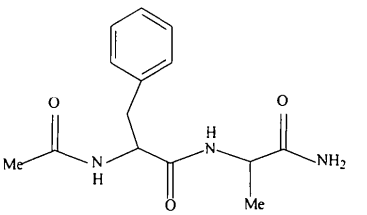
Abstract

The conformation of the peptide chain in *N*-acetyl-L-phenylalanyl-L-alaninamide (NAFAA), $C_{14}H_{19}N_3O_3$, is rather extended and falls in the *E* region of the φ, ψ map, according to the classification of Zimmerman, Pottle, Némethy & Scheraga [*Macromolecules* (1977), **10**, 1–9]. The values of φ, ψ torsion angles are like those of an antiparallel β pleated sheet. Side-chain conformation of Phe residue is defined by χ_1 = −174.5 (4)° and χ_2 = 105.5 (6)° and comes within the B_2 class of the observed statistical distribution for the aromatic residues in peptides [Cody, Duax & Hauptman, (1973). *Int. J. Peptide Protein Res.* **5**, 297–308]. Crystal packing is ruled by four intermolecular hydrogen bonds that involve all the donor groups, the acetyl O atom acting as a double acceptor. In the crystal there are ribbons of molecules translated along the *a* axis of the $P2_1$ space group and joined through three hydrogen bonds. The fourth hydrogen bond interconnects screw-related ribbons. The phenylalanyl rings stack parallel to the *a* direction with interplanar distances of 3.334 (7) Å.

Comment

X-ray studies on protected aminoacids and oligopeptides are useful for a better understanding of the conformational preferences of amino acid residues in biopolymers. The results obtained from small structures can also be used in the interpretation of refinement data of protein structures. As part of a program concerning crystallographic determinations and thermodynamic behaviour during the phase transitions of *N*-acetyl peptidoamides (Puliti, Barone, Giancola & Mattia, 1996; Puliti & Mattia, 1995, and references therein), we present here the X-ray structure of *N*-acetyl-L-phenylalanyl-L-alaninamide (NAFAA), (I).



(I)

A perspective view of the NAFAA molecule is shown in Fig. 1 together with the atomic labels used. The most significant values of the intramolecular geometry are reported in Table 2. Bond lengths and bond angles are generally in good agreement with the corresponding values reported in the literature for similar compounds (Ramachandran, Kolaskar, Ramakrishnan & Sasisekharan, 1974) and in particular for other *N*-acetylpeptidoamides (Puliti & Mattia, 1995, and references therein).

The molecule adopts a rather extended conformation. The peptide linkage is in a slightly distorted *trans* form [ω = 173.1 (4)°] and φ, ψ torsion angles for the two residues fall in the *E* region of the conventional Zimmerman map for peptides (Zimmerman, Pottle,

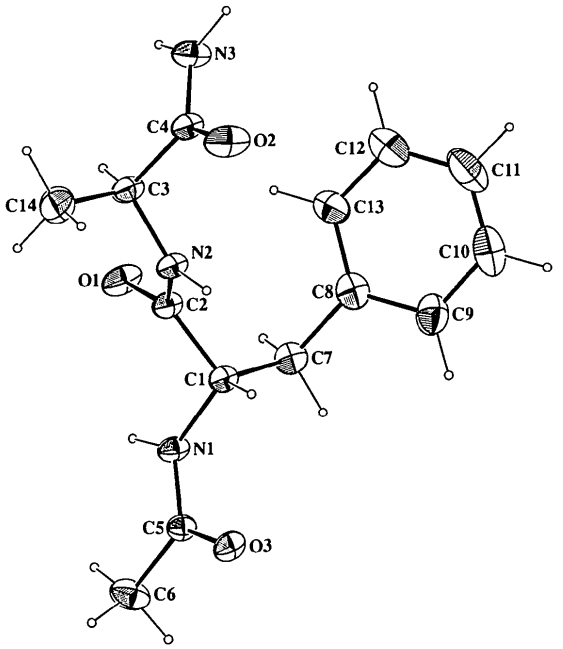


Fig. 1. Perspective view of the NAFAA molecule with the atomic labelling scheme. Displacement ellipsoids are plotted at the 30% probability level.

Némethy & Scheraga, 1977). Both φ, ψ pairs occur in the region of β chain conformations and are near the typical values for antiparallel β pleated sheets, $\varphi = -140°$, $\psi = 135°$ (Arnott, Dover & Elliott, 1967). The overall NAFAA conformation is not far from that of *N*-acetyl-L-alanyl-L-alaninamide (Puliti & Mattia, 1995).

The conformation of the Phe residue corresponds to the second of the three basic energy-minimum conformers defined by the three possible staggered values of $\chi_1 = 60$, 180 and $-60°$, respectively (Vàsquez, Némethy & Scheraga, 1983). The present *trans* conformation falls within the B_2 class, according to the statistical distribution of the observed conformations of aromatic residues (Cody, Duax & Hauptman, 1973). In the NAFAA molecule, the higher value of χ_2 compared with the minimum values from the energy calculations (105.5 instead of 78°) on the simple phenylalanine derivatives (Vàsquez *et al.*, 1983) is possible because of the lower observed value of ψ (129.5 instead of 151°). This is a clear proof of the ψ, χ_2 interdependence (Benedetti, Morelli, Némethy & Scheraga, 1983). In NAFAA, the shortest interactions between the ring and the backbone atoms are: C13···C2 = 3.166(7), C13···N2 = 3.361(7) Å.

Crystal packing is shown in Fig. 2. All of the H(N) atoms are involved in intermolecular hydrogen bonds, whose geometry is given in Table 3. Molecules translated along the *a* direction are linked into ribbons by means of three independent hydrogen bonds [N1—HN1···O3, N2—HN2···O1 and N3—HN3···O2]. The fourth hydrogen bond N3—H′N3···O3 interconnects the screw-related ribbons. The phenylalanyl rings stack parallel to the *a* direction (Fig. 3) with interplanar distances of 3.334(7) Å. The methyl groups of both alanine and acetoxy residues protrude from the molecular ribbons to face each other at alternate distances of 3.697(8) and 4.036(9) Å.

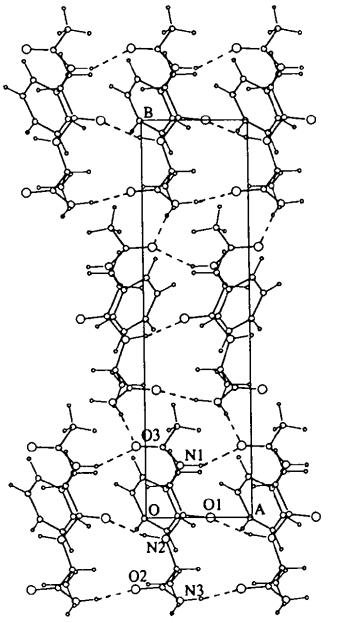


Fig. 2. Crystal packing projected on the *ab* plane. For clarity, only O and N atoms are labelled. Dashed lines indicate hydrogen bonds, the equivalent positions of acceptors are reported in Table 3.

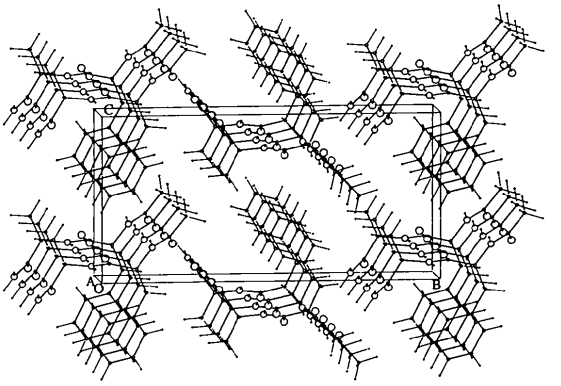


Fig. 3. View of the molecular arrangement showing the phenylalanyl stacking.

Experimental

The synthesis of *N*-acetyl-L-phenylalanyl-L-alaninamide (NAFAA) has been described previously (Milburn, 1984; Lilley, 1988).

Crystal data

$C_{14}H_{19}N_3O_3$
$M_r = 277.33$
Cu $K\alpha$ radiation
$\lambda = 1.54056$ Å

Monoclinic
$P2_1$
a = 4.809 (3) Å
b = 17.846 (4) Å
c = 8.825 (5) Å
β = 93.68 (3)°
V = 756 (1) Å^3
Z = 2
D_x = 1.218 Mg m^{-3}

Cell parameters from 25 reflections
θ = 20–25°
μ = 0.680 mm^{-1}
T = 293 K
Colourless
0.55 × 0.18 × 0.08 mm
Flattened prism

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: none
1580 measured reflections
1580 independent reflections
1105 observed reflections [$I > 2.5\sigma(I)$]

θ_{max} = 75°
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 22$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 240 min
intensity decay: 3%

Refinement

Refinement on F
R = 0.047
wR = 0.045
S = 0.93
1105 reflections
181 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + (0.01F_o)^2 + 0.1]$ (Killean & Lawrence, 1969)

$(\Delta/\sigma)_{max}$ <0.004
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: 7.5 (4) × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O1	0.6102 (5)	0.0	0.1684 (4)	5.52 (8)
O2	−0.1097 (6)	−0.1778 (2)	0.0068 (5)	7.04 (9)
O3	−0.0899 (5)	0.1815 (2)	0.2860 (4)	4.22 (6)
N1	0.3294 (6)	0.1324 (2)	0.2438 (4)	3.81 (7)
N2	0.1825 (6)	−0.0519 (2)	0.1438 (4)	3.67 (7)
N3	0.3112 (7)	−0.2082 (2)	−0.0655 (5)	5.6 (1)
C1	0.2281 (8)	0.0828 (2)	0.1217 (5)	3.61 (8)
C2	0.3539 (8)	0.0066 (3)	0.1492 (5)	3.79 (9)
C3	0.2817 (9)	−0.1285 (2)	0.1519 (6)	4.3 (1)
C4	0.1466 (8)	−0.1728 (3)	0.0231 (5)	4.2 (1)
C5	0.1657 (8)	0.1791 (2)	0.3144 (5)	3.53 (8)
C6	0.304 (1)	0.2301 (3)	0.4296 (6)	5.8 (1)
C7	0.3053 (9)	0.1151 (3)	−0.0301 (6)	4.9 (1)
C8	0.190 (1)	0.0731 (3)	−0.1694 (6)	5.6 (1)
C9	−0.031 (1)	0.1029 (4)	−0.2582 (7)	6.8 (2)
C10	−0.130 (2)	0.0641 (5)	−0.3891 (7)	8.9 (2)
C11	−0.018 (2)	−0.0014 (5)	−0.4279 (7)	9.9 (2)
C12	0.194 (2)	−0.0321 (5)	−0.3398 (7)	9.5 (2)
C13	0.296 (1)	0.0045 (4)	−0.2103 (6)	7.1 (2)
C14	0.221 (1)	−0.1643 (4)	0.3023 (7)	7.8 (2)

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

O1—C2	1.239 (4)	C3—C4	1.498 (6)
O2—C4	1.235 (5)	C3—C14	1.518 (8)
O3—C5	1.239 (4)	C5—C6	1.490 (7)
N1—C1	1.454 (5)	C7—C8	1.515 (7)
N1—C5	1.328 (5)	C8—C9	1.383 (8)
N2—C2	1.329 (5)	C8—C13	1.383 (9)
N2—C3	1.448 (6)	C9—C10	1.405 (9)
N3—C4	1.311 (6)	C10—C11	1.341 (9)
C1—C2	1.502 (6)	C11—C12	1.355 (9)
C1—C7	1.527 (7)	C12—C13	1.379 (9)
C1—N1—C5	123.3 (3)	N3—C4—C3	117.3 (4)
C2—N2—C3	122.5 (3)	O3—C5—N1	122.5 (4)
N1—C1—C2	108.7 (3)	O3—C5—C6	120.6 (4)
N1—C1—C7	109.3 (3)	N1—C5—C6	116.8 (3)
C2—C1—C7	111.4 (4)	C1—C7—C8	115.3 (4)
O1—C2—N2	122.7 (4)	C7—C8—C9	119.8 (5)
O1—C2—C1	119.7 (3)	C7—C8—C13	121.8 (5)
N2—C2—C1	117.6 (3)	C9—C8—C13	118.4 (5)
N2—C3—C4	109.6 (4)	C8—C9—C10	118.9 (6)
N2—C3—C14	111.0 (4)	C9—C10—C11	121.2 (6)
C4—C3—C14	110.1 (4)	C10—C11—C12	120.3 (7)
O2—C4—N3	122.2 (4)	C11—C12—C13	119.9 (7)
O2—C4—C3	120.5 (4)	C8—C13—C12	121.2 (6)

C5—N1—C1—C2	φ_1	−135.1 (4)
C5—N1—C1—C7		103.0 (4)
C1—N1—C5—C6	ω'	−175.8 (4)
C3—N2—C2—C1	ω	173.1 (4)
C2—N2—C3—C4	φ_2	−128.9 (4)
C2—N2—C3—C14		109.3 (5)
N1—C1—C2—N2	ψ_1	129.5 (4)
N1—C1—C7—C8	χ_1	−174.5 (4)
C2—C1—C7—C8		65.3 (5)
N2—C3—C4—N3	ψ_2	125.2 (4)
C1—C7—C8—C9	$\chi_{2,1}$	105.5 (6)
C1—C7—C8—C13	$\chi_{2,1}$	−73.6 (6)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D···A	H···A	D—H···A
N1—HN1···O3^{i}	2.928 (4)	2.05	150
N2—HN2···O1^{ii}	2.925 (4)	1.99	161
N3—HN3···O2^{i}	2.869 (4)	1.91	169
N3—H′N3···O3^{iii}	2.919 (5)	1.96	169

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

The equipment of the 'Centro di Biocristallografia' CNR-Napoli was used for the data collection. The structure was solved using the *SIR*92 package (Altomare *et al.*, 1993). All calculations were performed using *SDP* software (Enraf–Nonius, 1985) on a MicroVAX3100 computer.

The authors wish to thank Professor T. H. Lilley for the NAFAA samples.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1224). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2′-Deoxycytidine-*N*3-cyanoborane

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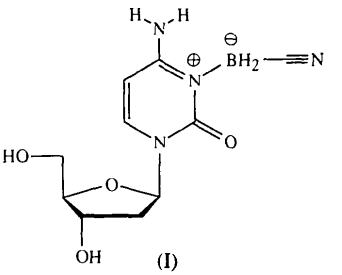
Abstract

The structure of the $P2_12_12_1$ form of 2′-deoxycytidine-*N*3-cyanoborane, $C_{10}H_{15}BN_4O_4$, has been determined. The sugar is in the ^2E puckering mode and the C5′—O5′ bond has a *tg* conformation while the relative orientation of the sugar and the base remains *anti*.

Comment

The bond lengths and angles of the title molecule, (I), in the $P2_12_12_1$ form described here are similar to those in the $P2_1$ form (Singh, Zottola, Ramsay Shaw & Pedersen, 1996). In the $P2_12_12_1$ form, the B atom is tetrahedral with bond angles ranging from 107.5 (2) to 110.1 (2)°. The B—C≡N moiety has a bent geometry as indicated by the angle 176.0 (3)°. Consistent with the $P2_1$ form, the exocyclic bond angle C4—N3—B, 124.3 (2)°, is larger than C2—N3—B, 115.5 (2)°. One of the BH_2 H atoms is in close van der Waals contact with one of the NH_2 H atoms (1.944 Å).



(I)

The cytosine ring is planar with the following deviations from the best least-squares plane, N1 −0.015 (2), C2 0.021 (2), N3 −0.009 (2), C4 −0.008 (2), C5 0.015 (3), C6 −0.003 (2) Å. The non-H substituents deviate significantly from the plane with C1′ out-of-plane by −0.155 (2), O2 by 0.029 (2), B31 by −0.102 (3) and N4 by −0.034 (2) Å. The torsion angles for the cytosine ring, ranging from 0.4 (3) to 3.7 (3)°, are in good agreement with the typical value obtained by Taylor & Kennard (1982) for a pyrimidine ring.

Unlike the $P2_1$ form, the furanose ring in the $P2_12_12_1$ form is in an envelope conformation with C2′ deviating 0.523 (3) Å from the plane containing the other four atoms and the ^2E puckering mode is assumed. The angle of pseudorotation P is −13.2° and ν_{max} is 18.8° (Saenger, 1984). In addition, the torsion angles C3′—C4′—C5′—O5′ 66.4 (3)° and O4′—C4′—C5′—O5′ −176.0 (2)°, demonstrate that the conformation around the exocyclic bond, C4′—C5′, is *tg*.

However, the torsion angle O4′—C1′—N1—C6 −14.6 (3)°, shows that the glycosyl conformation remains *anti*.

In the crystal, as shown in Fig. 2 and Table 2, molecules are linked through hydrogen bonds between bases, C5—H···O2 and N4—H···O2, to form infinite long chains along the *b* axis. These long chains are crosslinked by hydrogen bonds from sugar to sugar and from sugar to base, O5′—H···O3′ and O3′—H···N31, resulting in total in a three-dimensional hydrogen-bond network.

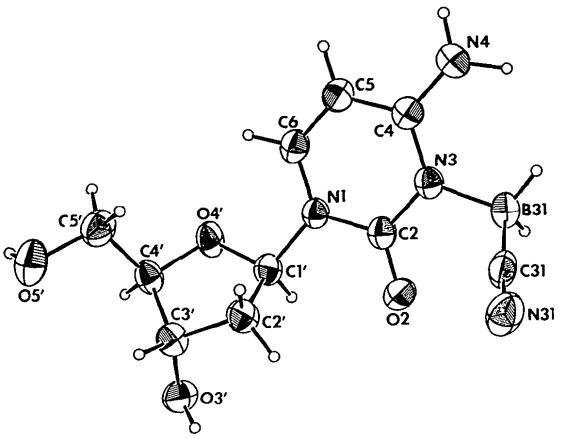


Fig. 1. Molecular structure of the title compound with displacement ellipsoids plotted at the 50% probability level.