

cell, including solvate molecules and intermolecular hydrogen bonding, as viewed down **b**, with **a** vertical and **c** horizontal, is illustrated in Fig. 2. Besides van der Waals interactions molecules of (+)-doronine are bound together in the crystal structure by a single hydrogen bond (2.802 Å) between O(24) and O(29). There are no other unusually short intermolecular distances.

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Structure of *N*-Acetyl-DL-phenylalanine *p*-Nitroanilide, C₁₇H₁₇N₃O₄

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Abstract. $M_r = 327.35$, triclinic, $P\bar{1}$, $a = 7.219$ (1), $b = 9.122$ (1), $c = 13.805$ (1) Å, $\alpha = 99.07$ (1), $\beta = 92.55$ (1), $\gamma = 111.41$ (1)°, $Z = 2$, $V = 830.55$ Å³, $T = 295$ K, $D_m = 1.307$ (3), $D_x = 1.309$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 0.7992$ mm⁻¹, $F(000) = 344$, $\lambda(\text{Cu } K\alpha_1) = 1.54060$ Å, final $R(F) = 0.054$ for 1903 reflections. The peptide-like groups of this chymotrypsin substrate are non-planar. The N–H···O- and C–H···O-type hydrogen bonds are a stabilizing factor in the molecule that exists in the extended conformation.

Introduction. *N*-Acetyl-DL-phenylalanine *p*-nitroanilide (APNA), a chymotrypsin substrate, is a molecule with two aromatic groups. The X-ray analysis of this compound was undertaken as part of the project on the structure of molecules of biological interest. The conformational analysis of APNA may provide useful information towards a better understanding of the conformation of peptides and amino acid derivatives. In this paper the conformation of APNA is compared with those of some other chymotrypsin substrates, such as *N*-glutaryl-L-phenylalanine *p*-nitroanilide (GPNA)

(Narasimhan & Pattabhi, 1982), *N*-acetyl-L-tyrosine *p*-nitroanilide (ATNA) (Michel & Durant, 1976), and *N*-acetyl-L-tyrosine ethyl ester (ATEE) (Pieret, Durant, Germain & Koch, 1972).

Experimental. Colourless needles (from an acetone–water mixture), 0.4 × 0.3 × 0.3 mm, Picker four-circle automatic diffractometer, graphite-monochromatized Cu $K\alpha$, $\theta/2\theta$ scan with line profile analysis (Grant & Gabe, 1978); data corrected for direct-beam polarization (Le Page, Gabe & Calvert, 1979) and Lorentz effects; unit-cell parameters determined from least-squares refinement of angles for 40 reflections with $40 < \theta < 50^\circ$; 2474 independent reflections with $\theta < 60^\circ$, 1903 with $I_{\text{net}} > 3\sigma(I_{\text{net}})$, no absorption correction, *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), anisotropic full matrix using F_o (Gantzel, Sparks & Trueblood, 1961), H (from ΔF synthesis) isotropic, final $R(F) = 0.054$, $R_w(F) = 0.054$ [Cruickshank's weighting scheme (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), $w = 1/(a + F_o + cF_o^2)$ where $a = 10.2$, $c = 0.003$], goodness of fit = 0.13; IBM 370/155 computer at the Indian Institute of Technology, Madras, India. Final refinement cycle Δ/σ (max) = 1.5, Δ/σ (mean) = 0.2, electron density in the final ΔF map $< 0.2 \text{ e } \text{Å}^{-3}$,

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atomic scattering factors from *International Tables for X-ray Crystallography* (1962); no correction for secondary extinction; other programs locally written in Madras.

Discussion. Final positional parameters with e.s.d.'s and equivalent isotropic B 's are listed in Table 1.*

The bond lengths and angles are shown in Fig. 1. The observed values of the bond lengths and angles for the nitro and phenyl groups conform to standard values except for those involving C(12), C(13) and C(14), which have very large thermal parameters. Similar effects were observed in *N*-acetyl-L-phenylalanyl-L-tyrosine (Stenkemp & Jensen, 1973) where the large thermal motion gave rise to unreliable bond lengths and angles in the aromatic ring. This also accounts for the large thermal parameters of H(C12), H(C13) and H(C14) in the aromatic ring. The thermal motion has affected the bond length C(11)–C(12) [1.333 (6) Å] and has also given rise to relatively large standard deviations in the bond lengths and angles for atoms C(11) through C(15). The thermal vibration of the terminal nitro group is also relatively large.

The conformation of the phenylalanine residue is defined by the torsion angles χ_1 , χ_{21} and χ_{22} . These torsion angles along with the corresponding values for GPNA, ATNA and ATEE are listed in Table 2. C(10) of the phenylalanine side chain takes the g^- conformation [N(3)–C(8)–C(9)–C(10) torsion

* Tables of anisotropic thermal parameters, observed and calculated structure factors, details of the least-squares planes, a list of torsion angles, and details of the hydrogen-bond scheme have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38794 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

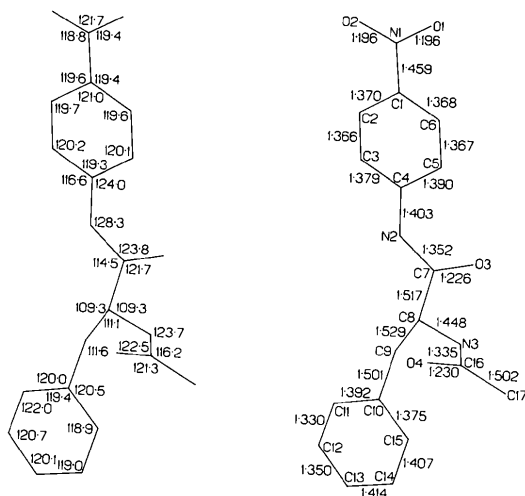


Fig. 1. Bond lengths (Å) and angles (°) observed in APNA; e.s.d.'s range from 0.003 to 0.0095 Å and from 0.2 to 0.5°.

angle is $-60.8(3)^\circ$] which agrees with the values in GPNA, *N*-(haloacetyl)-L-phenylalanyl-L-phenylalanine ethyl ester (Wei, Doherty & Einstein, 1972) and *D*-phenylalanyl-L-(*O*-methoxyphenylalanine) hydrobromide (Pattabhi & Venkatesan, 1970). The plane through C $^\alpha$ (8), C $^\beta$ (9) and C $^\gamma$ (10) makes an angle of $95.2(3)^\circ$ with the phenylalanine ring, which is close to the expected value of 90° . The notation followed is that of Edsall, Flory, Kendrew, Liquori, Nemethy, Ramachandran & Scheraga (1966).

Table 1. Fractional positional parameters ($\times 10^4$, for H $\times 10^3$) and isotropic temperature factors

For non-hydrogen atoms $B_{eq} = \frac{1}{3} \sum_i a_i a_j b_{ij}$.				
	x	y	z	$B_{eq}/B_{iso}(\text{Å}^2)$
C(1)	6176 (5)	3104 (4)	9529 (2)	4.9
C(2)	4921 (5)	1573 (4)	9113 (2)	5.6
C(3)	4067 (5)	1249 (3)	8161 (2)	4.7
C(4)	4467 (4)	2456 (3)	7619 (2)	3.9
C(5)	5712 (5)	4009 (4)	8058 (3)	5.5
C(6)	6569 (6)	4323 (3)	9009 (3)	5.7
C(7)	3710 (4)	2958 (4)	5961 (2)	4.1
C(8)	2589 (4)	2073 (3)	4956 (2)	3.8
C(9)	3987 (5)	1540 (4)	4316 (3)	4.9
C(10)	2937 (5)	618 (4)	3319 (3)	5.1
C(11)	1774 (5)	-1010 (4)	3198 (3)	6.3
C(12)	738 (7)	-1854 (6)	2340 (5)	9.5
C(13)	750 (8)	-1144 (8)	1552 (4)	8.7
C(14)	1902 (9)	507 (8)	1627 (4)	9.6
C(15)	3023 (7)	1387 (5)	2532 (3)	6.9
C(16)	-5 (4)	2654 (3)	4067 (2)	3.9
C(17)	-424 (5)	3825 (4)	3527 (3)	5.7
N(1)	7176 (5)	3429 (4)	10526 (2)	6.9
N(2)	3543 (3)	2020 (3)	6645 (2)	4.1
N(3)	1856 (3)	3114 (2)	4504 (2)	3.7
O(1)	8223 (6)	4774 (4)	10897 (2)	11.0
O(2)	6983 (7)	2329 (4)	10936 (2)	12.8
O(3)	4718 (4)	4399 (2)	6116 (2)	6.0
O(4)	-1318 (3)	1351 (2)	4102 (2)	5.0
H(C2)	464 (7)	88 (5)	950 (3)	6.7 (7)
H(C3)	323 (6)	12 (5)	783 (3)	3.3 (6)
H(C5)	598 (7)	487 (5)	769 (3)	4.7 (7)
H(C6)	750 (7)	541 (6)	938 (3)	5.4 (6)
H(C8)	150 (6)	121 (5)	501 (3)	1.7 (6)
H1(C9)	517 (6)	258 (5)	430 (3)	4.2 (7)
H2(C9)	438 (7)	97 (5)	468 (3)	4.3 (7)
H(C11)	180 (7)	-155 (6)	380 (4)	3.5 (6)
H(C12)	-6 (8)	-299 (7)	226 (4)	11.2 (12)
H(C13)	9 (9)	-174 (7)	96 (4)	10.0 (13)
H(C14)	217 (9)	109 (7)	116 (4)	9.1 (10)
H(C15)	392 (7)	239 (6)	257 (4)	4.4 (7)
H1(C17)	-170 (7)	384 (5)	364 (3)	7.8 (8)
H2(C17)	55 (7)	485 (5)	373 (3)	6.1 (7)
H3(C17)	-54 (7)	352 (5)	289 (3)	9.1 (10)
H(N2)	280 (6)	100 (5)	642 (3)	4.2 (6)
H(N3)	271 (6)	403 (5)	448 (3)	4.8 (6)

Table 2. Torsion angles (°) compared with corresponding angles of GPNA, ATNA and ATEE

		APNA	GPNA	ATNA	ATEE
N(3)–C(8)–C(9)–C(10)	χ_1	-60.8 (3)	-61.2 (6)	-69.3	-62.9
C(8)–C(9)–C(10)–C(11)	χ_{21}	-82.8 (3)	109.5 (7)	107.3	117.5
C(8)–C(9)–C(10)–C(15)	χ_{22}	93.6 (3)	-68.6 (7)	-74.4	-64.0
N(3)–C(8)–C(7)–O(3)	ψ_1	-35.4 (3)	-18.9 (8)	-80.5	-16.4
N(3)–C(8)–C(7)–N(2)	ψ_2	146.4 (2)	162.8 (5)	100.2	164.4
C(17)–C(16)–N(3)–C(8)	ω	-172.5 (2)	179.7 (5)	–	–

APNA: *N*-Acetyl-DL-phenylalanine *p*-nitroanilide (present study). GPNA: *N*-Glutaryl-L-phenylalanine *p*-nitroanilide. ATNA: *N*-Acetyl-L-tyrosine *p*-nitroanilide. ATEE: *N*-Acetyl-L-tyrosine ethyl ester.

The groups of atoms [C(8),O(3),C(7),N(2),C(4)] and [C(8),N(3),C(16),O(4),C(17)] can be compared with a peptide group (Narasimhan & Pattabhi, 1982) and the torsion angles ψ_1 [N(3)—C(8)—C(7)—O(3)] and ψ_2 [N(3)—C(8)—C(7)—N(2)] are $-35.4(3)$ and $146.4(2)^\circ$ respectively. The corresponding values for GPNA, ATNA and ATEE are listed in Table 2 for comparison. The least-squares planes through these groups deviate significantly from planarity (χ^2 values are 953.7 and 153.0 respectively). Similar nonplanarity was reported earlier (Stenkemp & Jensen, 1973) but in GPNA one of the two peptide groups is planar within the limits of experimental error. The bond lengths and angles in this region agree with those of peptide dimensions (Marsh & Donohue, 1967). The group C(8), N(3), C(16) and C(17) is in the *trans* configuration with a torsion angle ω [C(8)—N(3)—C(16)—C(17)] of $-172.5(2)^\circ$.

The phenyl ring of the nitroanilide group deviates slightly from planarity ($\chi^2 = 17.8$). This nonplanarity (though small) could possibly be due to the short intermolecular contact (3.22 Å) between C(12) and O(1) which pulls the nitro group away from the plane of the phenyl group. The least-squares plane through the nitro group makes an angle of $6.1(3)^\circ$ with the plane through the phenyl ring. The angle between the two phenyl-ring planes is $3.6(3)^\circ$.

The crystal packing of the molecules projected down the *a* axis is shown in Fig. 2. The molecule is in an extended conformation with the centers of the phenyl groups of the phenylalanine and nitroanilide moieties separated by 8.55 Å. There are two N—H...O-type intermolecular hydrogen bonds. The N(3)...O(3) and N(2)...O(4) bond distances are 2.949(3) and 2.889(3) Å and the corresponding hydrogen-bond angles are $155(3)$ and $175(3)^\circ$ respectively. The H(N3)...O(3) and H(N2)...O(4) distances are 2.15(4) and 2.01(4) Å respectively. The intermolecular distance of 3.224(6) Å between C(12) and O(1) indicates a C—H...O-type of interaction. Such bonds initially suggested by Sutor (1962) and more recently by Taylor & Kennard (1982) were observed in GPNA and other similar structures. The H(C12)...O(1) distance is 2.44(5) Å and the C(12)—H(C12)...O(1) bond angle is $137(4)^\circ$.

VP is a UGC (India) Career awardee.

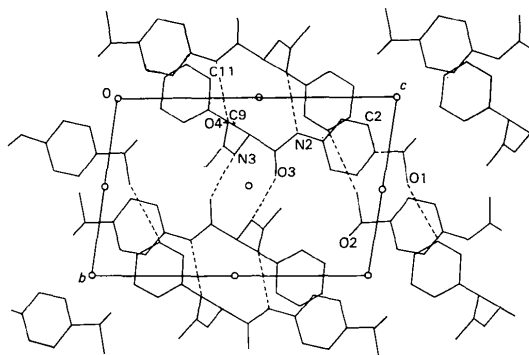


Fig. 2. Packing of the molecules down the *a* axis.

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