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**N-Acetyl-L-tyrosine-p-nitroanilide**

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**Abstract.**  $C_{17}H_{17}N_3O_5$ ; M.W. 343.34; orthorhombic, space group  $P2_12_12_1$ ;  $a=15.621$ ,  $b=19.941$ ,  $c=5.253$  Å;  $D_m=1.394$ ,  $D_c=1.393$  g cm $^{-3}$  for  $Z=4$ .  $R=0.058$  for 1496 observed reflexions. The structure is compared with that of acetyltyrosine ethyl ester.

**Introduction.** The crystal was colourless and cut into a needle elongated on  $b$  ( $0.2 \times 0.2 \times 0.4$  mm). The space group was determined from precession photographs and confirmed on a CAD-4 Nonius automatic diffractometer. 1905 reflexions were measured with Cu  $K\alpha$

radiation by the  $\omega$ - $2\theta$  scan method. One standard intensity was counted every 50 reflexions. No fluctuation was observed. In the range  $2\theta \leq 140^\circ$ , 1496 reflexions had intensities greater than  $2.5\sigma$  above background, where  $\sigma(I)$  is defined by  $\sigma^2(I) = S + B + (0.03S)^2$ ,  $S$  being the scan and  $B$  the background count. Lorentz and polarization factors were applied, but no absorption correction.  $E$  statistics confirmed the non-centrosymmetric space group. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Phases of 240  $E$ 's with  $|E| \geq 1.4$

Table 1. *Parameters derived from the final least-squares refinement (all  $\times 10^4$ )*

The expressions used for the temperature factors are:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)] \text{ and } \exp[-2\pi^2U(2 \sin \theta/\lambda)^2].$$

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O(1)	1177 (3)	4044 (2)	9412 (9)	699 (28)	347 (20)	578 (26)	68 (19)	-166 (25)	-78 (20)
O(2)	2176 (3)	3140 (2)	1963 (9)	610 (27)	637 (28)	446 (26)	100 (21)	-73 (24)	67 (24)
O(3)	8634 (3)	3168 (2)	1472 (8)	1174 (37)	345 (20)	314 (22)	-222 (23)	-43 (26)	53 (18)
O(4)	5983 (5)	3510 (2)	8671 (18)	1593 (65)	391 (28)	1726 (78)	-20 (34)	-750 (66)	-213 (40)
O(5)	6579 (5)	3498 (2)	2279 (18)	1722 (71)	462 (30)	1337 (65)	224 (36)	-249 (63)	285 (40)
N(1)	2452 (2)	2838 (2)	5998 (9)	373 (24)	349 (22)	403 (26)	38 (18)	17 (21)	50 (22)
N(2)	8652 (3)	3395 (2)	5714 (8)	516 (25)	307 (20)	273 (22)	-28 (19)	23 (21)	36 (18)
N(3)	6279 (3)	3788 (2)	478 (16)	558 (31)	333 (27)	933 (50)	20 (24)	63 (36)	70 (34)
C(1)	1208 (3)	4700 (2)	173 (10)	462 (27)	319 (24)	358 (28)	12 (21)	-4 (24)	-27 (22)
C(2)	760 (3)	5157 (2)	8698 (11)	427 (27)	399 (26)	413 (29)	-25 (23)	-49 (26)	12 (26)
C(3)	4260 (3)	4175 (2)	4393 (12)	438 (30)	379 (26)	445 (30)	18 (23)	74 (28)	-39 (26)
C(4)	3837 (3)	3947 (2)	6558 (11)	374 (25)	326 (25)	433 (30)	-13 (20)	-46 (26)	16 (23)
C(5)	3376 (3)	4410 (2)	7976 (12)	458 (30)	395 (28)	389 (31)	-38 (24)	15 (27)	27 (26)
C(6)	1648 (3)	4914 (2)	2310 (12)	543 (32)	367 (27)	408 (31)	62 (23)	-84 (29)	11 (25)
C(7)	3902 (3)	3221 (2)	7344 (12)	470 (31)	337 (28)	516 (32)	3 (22)	-107 (28)	58 (26)
C(8)	3372 (3)	2747 (2)	5657 (11)	483 (32)	291 (22)	387 (28)	94 (21)	27 (25)	63 (22)
C(9)	1917 (3)	2996 (2)	4125 (13)	479 (33)	253 (24)	523 (38)	1 (23)	-22 (31)	-34 (25)
C(10)	977 (3)	3007 (3)	4764 (16)	336 (28)	684 (39)	767 (49)	6 (28)	-24 (31)	-107 (38)
C(11)	8569 (3)	2983 (2)	3677 (11)	466 (30)	338 (27)	394 (32)	-82 (24)	-46 (28)	86 (24)
C(12)	8709 (3)	4099 (2)	5609 (11)	357 (28)	326 (24)	303 (27)	-17 (22)	-21 (25)	24 (24)
C(13)	8328 (3)	4458 (2)	7589 (11)	468 (30)	442 (28)	380 (27)	-4 (23)	49 (27)	0 (25)
C(14)	6672 (3)	4846 (3)	2577 (12)	428 (30)	487 (30)	463 (32)	85 (25)	-1 (29)	74 (30)
C(15)	6263 (3)	4526 (2)	583 (12)	447 (29)	293 (23)	545 (33)	-10 (21)	50 (28)	64 (25)
C(16)	5851 (3)	4867 (2)	8650 (12)	456 (28)	367 (28)	502 (31)	-80 (24)	-4 (28)	-6 (26)
C(17)	9135 (3)	4434 (2)	3651 (11)	405 (26)	346 (23)	398 (28)	-46 (21)	58 (26)	-31 (24)

Table 1 (cont.)

	x	y	z	U
H(100)	1530 (32)	3749 (23)	655 (114)	684
H(201)	2227 (30)	2744 (25)	7581 (116)	390
H(202)	8630 (31)	3163 (24)	7577 (116)	457
H(2)	4594 (29)	5039 (25)	2154 (118)	412
H(3)	4641 (31)	3819 (24)	3510 (111)	456
H(5)	3136 (32)	4248 (23)	9595 (107)	449
H(6)	1936 (32)	4610 (24)	3420 (106)	533
H(71)	447 (29)	6945 (25)	2132 (116)	488
H(72)	1246 (32)	6816 (24)	4137 (110)	488
H(8)	3471 (31)	2850 (23)	3893 (110)	488
H(110)	697 (32)	3459 (25)	4584 (111)	330
H(210)	4565 (30)	7260 (25)	8573 (115)	330
H(310)	4246 (32)	7064 (24)	1667 (108)	330
H(13)	8043 (33)	4237 (25)	8677 (116)	466
H(14)	6901 (34)	4584 (25)	4052 (113)	456
H(16)	5506 (30)	4596 (25)	7284 (114)	441
H(17)	9416 (31)	4176 (25)	2208 (115)	416

were assigned and 64 sets of phases generated. A partial structure containing 9 atoms was used; a subsequent Fourier refinement improved the atomic coordinates till  $R$  was 0.25. Scattering factors were those of

Cromer & Mann (1968) for non-hydrogen atoms, and Stewart, Kruger, Ammon, Dickinson & Hall (1972) for H. The structure was refined by the full-matrix least-squares program *CRYLSQ* of the X-RAY 72 system. H atoms were revealed by difference synthesis. The final  $R$  was 0.058, with anisotropic temperature factors for all non-H atoms. Final atomic positions and temperature factors are given in Table 1.\* Fig. 1 and Table 2 give intramolecular bond lengths and angles.

**Discussion.** The enzymatic hydrolysis of acetyltyrosine-nitroanilide (ATNA) by  $\alpha$ -chymotrypsin has been investigated (Bundy, 1963). The author postulated that the conformation of this substrate should take a prominent part in the association with the enzyme. Thus the conformational analysis of ATNA was

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31614 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

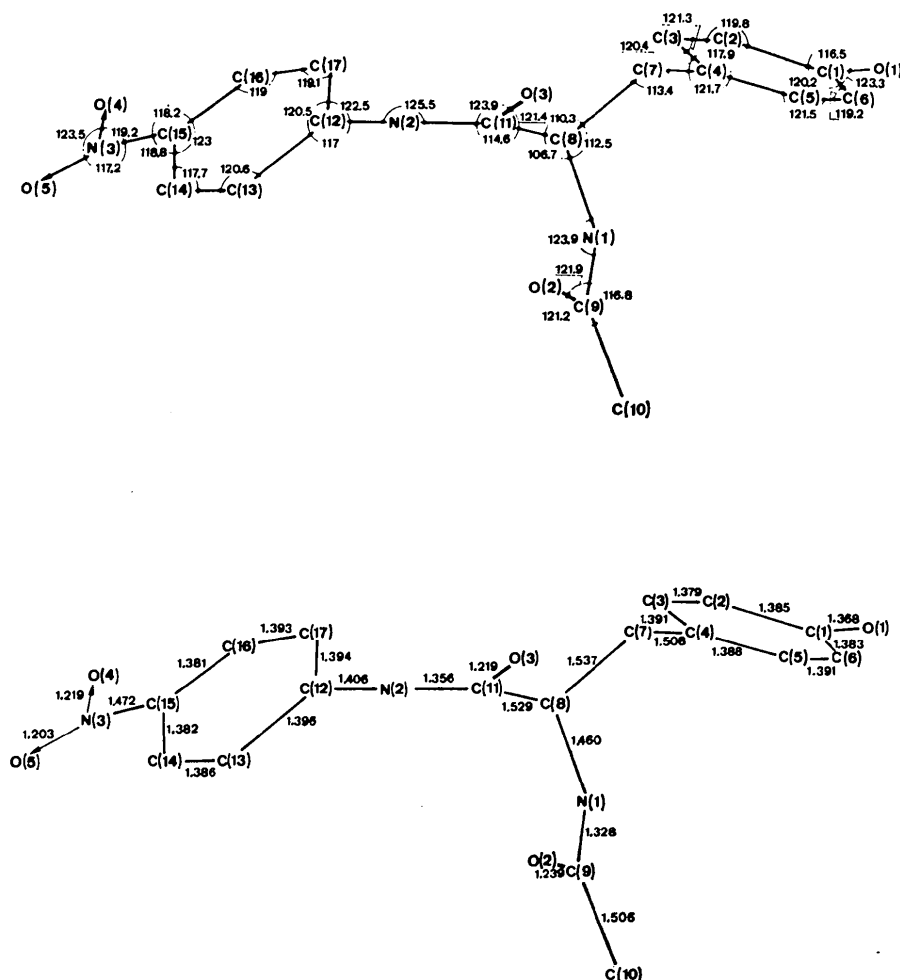


Fig. 1. Numbering, intramolecular distances and angles. (Highest value for  $\sigma = 0.008$  Å.)

Table 2. Distances (Å)  
and angles (°) involving H atoms

O(1)—H(100)	1.03 (5)	C(8)—H(8)	0.96 (5)
N(1)—H(201)	0.92 (5)	C(10)—H(110)	1.00 (5)
N(2)—H(202)	1.08 (5)	C(10)—H(210)	1.06 (5)
C(2)—H(2)	1.05 (5)	C(10)—H(310)	1.18 (5)
C(3)—H(3)	1.03 (5)	C(13)—H(13)	0.88 (5)
C(5)—H(5)	0.98 (5)	C(14)—H(14)	1.00 (5)
C(6)—H(6)	0.95 (5)	C(16)—H(16)	1.04 (5)
C(7)—H(71)	1.07 (4)	C(17)—H(17)	1.01 (5)
C(7)—H(72)	0.97 (5)		
C(1)—C(1)—H(100)	109 (2)	H(71)—C(7)—H(72)	107 (4)
C(9)—N(1)—H(201)	117 (3)	N(1)—C(8)—H(8)	104 (3)
C(8)—N(1)—H(201)	118 (5)	C(7)—C(8)—H(8)	109 (3)
C(11)—N(2)—H(202)	116 (3)	C(11)—C(8)—H(8)	113 (3)
C(12)—N(2)—H(202)	117 (3)	C(9)—C(10)—H(110)	114 (3)
C(1)—C(2)—H(2)	116 (3)	C(9)—C(10)—H(310)	121 (3)
C(3)—C(2)—H(2)	123 (3)	H(110)—C(10)—H(210)	97 (4)
C(2)—C(3)—H(3)	128 (3)	H(110)—C(10)—H(310)	97 (4)
C(4)—C(4)—H(3)	114 (3)	H(310)—C(10)—H(210)	101 (3)
C(4)—C(5)—H(5)	116 (3)	H(210)—C(10)—C(9)	125 (3)
C(6)—C(5)—H(5)	121 (3)	C(12)—C(13)—H(13)	117 (3)
C(1)—C(6)—H(6)	122 (3)	C(13)—C(14)—H(14)	120 (3)
C(5)—C(6)—H(6)	118 (3)	C(15)—C(14)—H(14)	121 (3)
C(4)—C(7)—H(71)	109 (3)	C(15)—C(16)—H(16)	119 (3)
C(4)—C(7)—H(72)	108 (3)	C(17)—C(16)—H(16)	121 (3)
C(8)—C(7)—H(71)	104 (3)	C(12)—C(17)—H(17)	120 (3)
C(8)—C(7)—H(72)	112 (3)	C(16)—C(17)—H(17)	120 (3)

performed in the framework of a more general study of substrates of  $\alpha$ -chymotrypsin. We compare here the structure of ATNA with that of acetyltyrosine ethyl ester (ATEE). Dihedral angles are given in Table 3.

Table 3. Torsion angles, compared with corresponding angles of acetyltyrosine ethyl ester (Pieret, Durant, Germain & Koch, 1972)

Torsional parameters are computed from authors' coordinates changed to correspond to the L-isomer.

	N-Acetyl- L-tyrosine- <i>p</i> -nitro- anilide	N-Acetyl- L-tyrosine ethyl- ester
$\psi_1$ [N(1)—C(8)—C(11)—O(3)]	-80.5°	-16.4°
$\psi_2$ [N(1)—C(8)—C(11)—N(2)]	100.2	164.4
[C(11)—C(8)—N(1)—C(9)]	-116.5	-75.2
$\chi_1$ [N(1)—C(8)—C(7)—C(4)]	-69.3	-62.9
$\chi_{21}$ [C(8)—C(7)—C(4)—C(5)]	107.3	117.5
$\chi_{22}$ [C(8)—C(7)—C(4)—C(3)]	-74.4	-64.0
O(2)—C(9)—N(1)—C(8)	-6.7	-3.2
C(8)—C(11)—N(2)—C(12)	-170.4	180.0
C(11)—N(2)—C(12)—C(13)	144.6	
C(16)—C(15)—N(3)—O(4)	3.8	

The conformation of the tyrosine residue is defined by the torsional angles  $\chi_1$ , the angle between the N(1)—C(8)—C(7) and C(8)—C(7)—C(4) planes; and  $\chi_2$ , which describes the relative orientation of the aromatic ring and the C(8)—C(7)—C(4) plane.

In both molecules, we observe no significant difference in these angles: the tyrosine residue lies in an extended conformation. N(1) and C(11) are in the

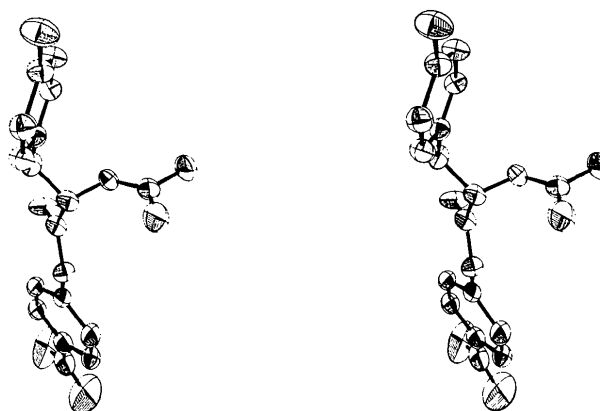


Fig. 2. ORTEP stereo diagram with non-hydrogen atoms represented by thermal ellipsoids at 50% probability.

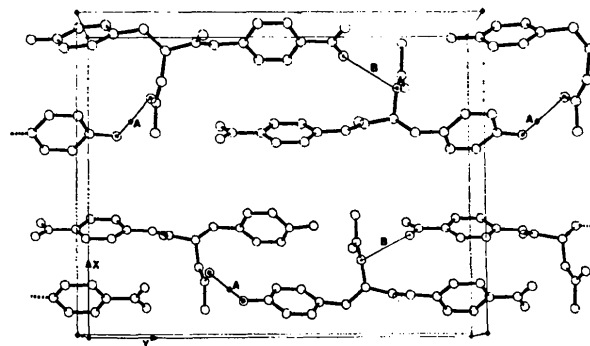


Fig. 3. View of the unit cell along *c*.

same position, relative to the phenolic ring, for both molecules as well as the orientation of the *N*-acetyl group [O(2)—C(9)—N(1)—C(8)]. The only appreciable modification is the rotation around C(8)—C(11) ( $\psi_1$  and  $\psi_2$ ), probably due to intermolecular interactions which are different for nitroanilide and ethyl ester groups.

Packing is shown in Fig. 3.  $A = 2.72$  Å and corresponds to an H bond: C(9)=O(2)···H(100)—O(1).  $B = 3.13$  Å is a van der Waals interaction. Such parallel columns of molecules along *b* are connected together by van der Waals interactions.

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