Fig. 3. Views of the unit cell along b and c.

Because of the absence of proton donors in the molecule, short intermolecular distances are not expected.

Packing by interaction between aromatic rings ($A = 3.65$ Å) is shown in Fig. 3. The shortest intermolecular distances ($B = 3.35$ Å) are van der Waals contacts between ester groups. This network of intermolecular bonds is very loose and must be related to the low melting point (91°) compared with that of the analogous compound where –CO– is substituted by –NH– (139°).

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D-Methyl 3,4-Dihydroisocarbostyril-3-carboxylate

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Abstract. $C_{11}H_{11}O_3N$; M.W. 205.2; oithorhombic, space group $P2_12_12_1$; $a = 8.914$, $b = 21.050$, $c = 5.398$ Å; $D_m = 1.350$, $D_c = 1.346$ g cm^{-3} for $Z = 4$. $R = 0.042$ for 849 observed reflexions. The structure is compared with those of related enzyme substrates.

Introduction. The crystal, $0.3 \times 0.3 \times 0.5$ mm, was centred on the goniometer and treated automatically. With the SEARCH and INDEX routines of the CAD-4 Nonius system, the space group and crystallographic parameters were determined; Table 1 gives experimental conditions for the data collection. 1199 reflexions were measured and 849 had intensities greater than 2.5σ above background; Lorentz and polarization factors were applied, but no absorption correction. For the non-hydrogen atoms, the scattering factors were those of Cromer & Mann (1968), and Stewart, Kruger, Ammon, Dickinson & Hall (1972) for H. The

structure was solved by direct methods: the phases of 450 normalized structure factors with $E > 1.5$ were assigned with MULTAN (Germain, Main & Woolfson, 1971). The Fourier transform of one of the 16 most probable sets gave the position of all the non-hydrogen atoms. Fourier refinement improved the atomic coordinates till R was 23%. Full-matrix least-squares refinement was then performed with CRYLSQ from the X-RAY 72 system.

Table 1. Experimental conditions

Source: Cu $K\bar{\alpha}$, $\lambda = 1.5418$ Å: ω–2θ scan
Graphite monochromator
Scanning (°): $0.7 + 0.25$ tg θ
θ min: 2°; θ max: 72°
Aperture: $3.0 + 0.5$ tg θ
Confidence level: 2.5σ
Total number of independent reflexions: 1199
Total observed: 849

Table 2. *Parameters derived from the final least-squares refinement (all $\times 10^4$)*

The expressions used for the temperature factors are:

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	8145 (4)	4450 (1)	8078 (8)	560 (18)	311 (15)	688 (24)	34 (15)	20 (19)	−80 (16)
O(1)	−9186 (4)	4263 (2)	5558 (7)	777 (22)	1126 (29)	489 (18)	−177 (21)	119 (20)	−25 (20)
O(2)	−7935 (4)	4236 (1)	9122 (7)	476 (15)	718 (18)	678 (20)	−62 (14)	68 (16)	58 (17)
O(3)	6465 (3)	4283 (1)	5004 (6)	524 (15)	435 (14)	792 (22)	−26 (12)	−59 (17)	143 (15)
C(1)	7358 (4)	4078 (2)	6539 (8)	387 (18)	331 (16)	578 (22)	−2 (13)	102 (19)	6 (17)
C(2)	7588 (4)	3399 (1)	6894 (7)	377 (16)	329 (15)	439 (18)	−24 (13)	55 (16)	16 (14)
C(3)	6861 (5)	2993 (2)	5299 (8)	523 (22)	408 (22)	511 (23)	−115 (18)	17 (21)	2 (18)
C(4)	7059 (7)	2348 (2)	5558 (11)	761 (30)	393 (22)	698 (32)	−123 (22)	78 (30)	15 (22)
C(5)	7980 (5)	2131 (2)	7433 (10)	786 (28)	312 (17)	779 (29)	−27 (20)	177 (28)	41 (21)
C(6)	8694 (5)	2528 (2)	9035 (9)	587 (22)	388 (18)	603 (24)	−17 (17)	72 (22)	143 (19)
C(7)	8510 (4)	3175 (1)	8187 (7)	441 (18)	376 (17)	405 (18)	−34 (14)	101 (16)	23 (15)
C(8)	9200 (5)	3621 (2)	9411 (8)	580 (23)	518 (22)	394 (19)	−98 (19)	33 (21)	13 (17)
C(9)	9452 (4)	4255 (2)	9420 (8)	512 (22)	372 (17)	495 (21)	−40 (16)	41 (20)	−114 (18)
C(10)	9165 (5)	4255 (2)	7758 (9)	525 (21)	332 (17)	601 (25)	−77 (16)	65 (21)	−41 (18)
C(11)	6317 (6)	4252 (3)	7823 (15)	519 (26)	768 (34)	1016 (47)	−104 (26)	226 (31)	−22 (40)

Table 2 *(cont.)*

	x	y	z	U
H(111)	3645 (69)	3952 (31)	6196 (122)	1026 (241)
H(112)	5755 (67)	9403 (28)	5774 (142)	1132 (222)
H(113)	4528 (73)	4260 (31)	8899 (134)	1069 (242)
H(1)	7762 (49)	4938 (23)	8328 (100)	697 (153)
H(3)	3943 (53)	8137 (20)	1024 (98)	683 (139)
H(4)	6501 (84)	2015 (34)	4312 (163)	1071 (321)
H(5)	3081 (49)	3321 (23)	2450 (95)	735 (137)
H(6)	5498 (49)	7654 (21)	5446 (95)	701 (137)
H(81)	9769 (50)	8479 (19)	3696 (88)	627 (130)
H(82)	6397 (58)	6312 (24)	6971 (106)	837 (174)
H(9)	9637 (50)	4582 (21)	956 (100)	634 (131)

H atoms were revealed by a difference synthesis. With anisotropic temperature factors for all non-hydrogen atoms and isotropic for H [$\{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$] was 0·055, where $w = 1·0/(AF_o + BF_o^2 + BF_o^2 + CF_o^3)$ with $A = 2F_o^{min} = 5·0$, $B = 2/F_o^{max} = 0·0016$, $C = 0$.

The final R was 0·042. Final atomic positions and temperature factors are given in Table 2; Fig. 1 gives bond lengths and angles.*

Discussion. The enzymatic hydrolysis of locked substrates by α-chymotrypsin requires geometric and electronic conditions which have been investigated earlier (Pattabiraman & Lawson, 1972). In order to define the conformational parameters of the ideal substrate of α-chymotrypsin, we have determined the crystal structure of D-methyl 3,4-dihydroisocarbostyril-3-carboxylate. This compound is the most reactive in the series of known locked substrates of serine enzymes. The most important feature of the molecular structure is
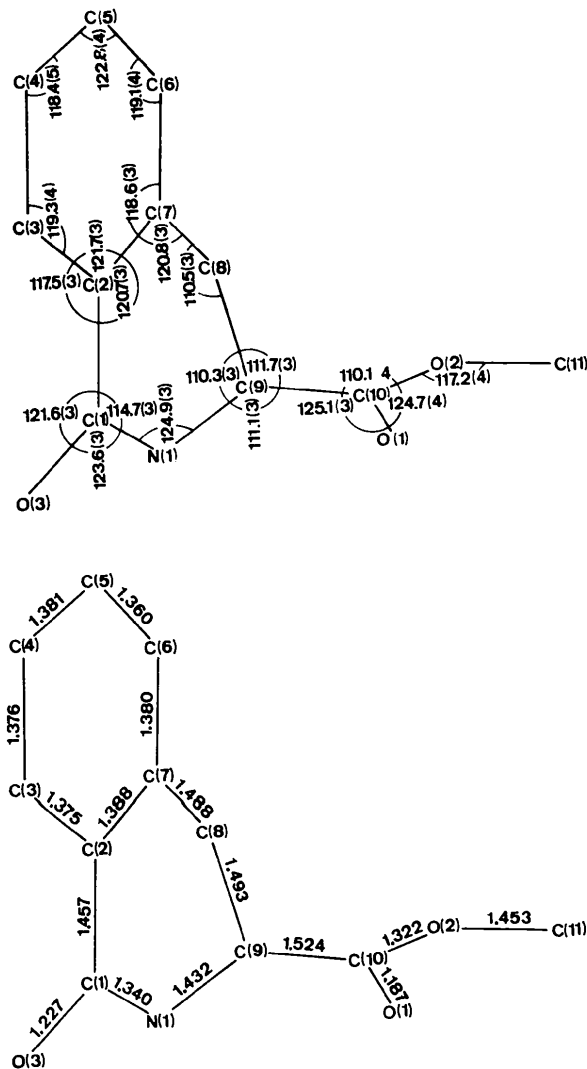
Fig. 1. Numbering, intramolecular distances and angles. $\sigma = 0·005$ for C–C and 0·004 Å for C–N and C–O.
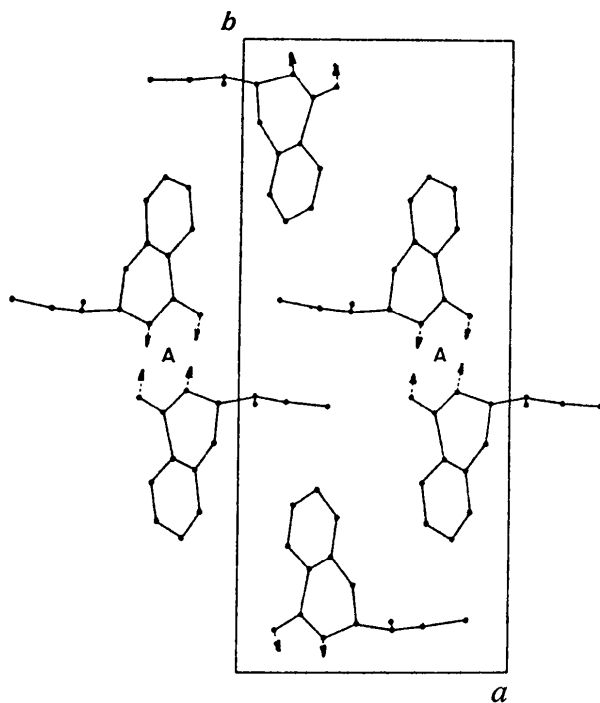
Table 3. *Torsion angles, compared with corresponding angles in methyl dihydroisocoumarin-3-carboxylate and acetyltyrosine ethyl ester*

Methyl dihydroisocarbostyril-3-carboxylate		Methyl dihydroisocoumarin-3-carboxylate		Acetyltyrosine ethyl ester	
C(9)–C(8)—C(7)–C(2)	28·7	C(9)–C(8)—C(7)-C(2)	30·0	χ_{21}	62·6
C(9)–C(8)—C(7)–C(6)	206·0	C(9)–C(8)—C(7)–C(6)	210·0	χ_{22}	243·9
N(1)–C(9)—C(8)–C(7)	45·8	O(4)–C(9)—C(8)–C(7)	−56·5	χ_1	−62·9
O(2)-C(10)-C(9)–N(1)	163·9	O(2)-C(10)-C(9)-O(4)	170·0	ψ_1	164·4
O(1)-C(10)-C(9)–N(1)	343·2	O(1)-C(19)-C(0)-O(4)	351·0	ψ_2	343·6
C(1)–N(1)—C(9)–C(10)	78·8	C(1)-O(4)—C(9)-C(10)	189·5	ϕ	75·2
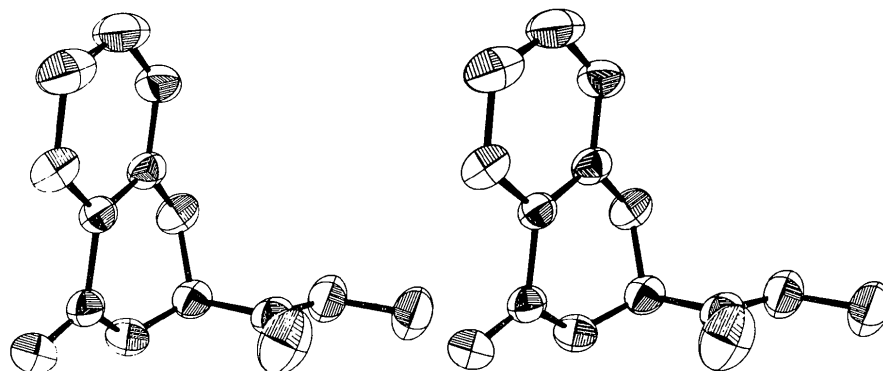
Fig. 2. *ORTEP* stereodiagram with non-hydrogen atoms represented by thermal ellipsoids at 50 % probability.

the position of C(10) with respect to the aromatic ring; Fig. 2 shows that the carboxylate group is oriented in an axial position. Dihedral angles are compared with

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

those in acetyltyrosine ethyl ester (Pieret, Durant, Germain & Koch, 1972) and methyl 3,4-dihydroisocoumarin-3-carboxylate (Michel & Durant, 1976) in Table 3. Deviations from coplanarity with the aromatic ring for different atoms are given in Table 4. Short intermolecular distances ($A = 2·883$ Å) are shown on Fig. 3; they correspond to hydrogen bonds between N(1) and O(3). These interactions generate helical columns of molecules; the packing between columns corresponds to van der Waals contacts.

Table 4. *Deviations* (Å) *of atoms from the aromatic ring*

The plane is: $0·7852x + 0·0368y + -0·6181z - 3·2689 = 0$
Atoms in plane: C(2) C(3) C(4) C(5) C(6) C(7)

Deviations of atoms in plane

C(2)	0·0054	C(5)	0·0015
C(3)	−0·0027	C(6)	0·0011
C(4)	−0·0007	C(7)	−0·0046

Deviations of the other atoms

C(8)	−0·0816	O(1)	2·7765
C(9)	0·5341	O(2)	2·4611
C(10)	2·0565	O(3)	−0·0814
C(11)	3·8948	N(1)	0·0820
C(1)	0·0514		

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Thallium Lead Hexanitrocuprate(II) at 295 K

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Abstract. $Tl_2PbCu(NO_2)_6$, cubic, $Fm3$, $a = 10.7344$ (5) Å at 295 K ($\lambda = 0.70926$ Å), $Z = 4$, $D_x = 5.131$ g cm^{-3}. It is isomorphous with $K_2PbCu(NO_2)_6$ at 295 K. The hexanitrocuprate(II) ion has $m3$ symmetry with a Cu–N bond length of 2.118 (6) Å. The N–O bond distance is 1.252 (4) Å and the O–N–O angle is 116.6 (5)°.

Introduction. The greenish-black crystals of $Tl_2PbCu(NO_2)_6$ were grown by slow cooling (1°/h) of a saturated solution at 50° (Reinen, Friebel & Reetz, 1972). Laue symmetry, systematic absences (*hkl* with $h+k$, $k+l$, or $h+l$ odd) and the expected structure indicate the space group $Fm3$.

The spherical data crystal was obtained by grinding in an abrasion chamber. The average diameter of the crystal was 0.1670 mm with a maximum of 0.1825 and a minimum of 0.1555 mm. The cell constants were determined from least-squares refinement of 2θ, ω, and χ values for 18 Mo $K\alpha_1$ reflections measured at 2θ angles of about 47°.

A four-circle automated diffractometer was used to collect intensity data at 295 K for 3143 reflections out to $2\theta = 90°$ (Nb-filtered Mo $K\alpha$ radiation $12° < 2\theta < 90°$ and Zr-Y balanced filters $0° < 2\theta < 12°$). The 2θ step

scan mode provided in the diffractometer control program (Lenhert, 1975) was used. The 2θ scan range included the usual constant factor and the 2θ dependent dispersion factor; the number of steps was adjusted automatically so that 25 steps per degree were used for all reflections. 2825 reflections from the *hkl* and $-h,-k,-l$ octants were measured with 4 s step counts and two 40 s background measurements at the limits of the 2θ scan. In order to reduce the influence of unobserved reflections on the refined parameters and on the electron density map an additional 318 weak reflections were remeasured in other octants with 10 s step counts and 100 s background measurements. All observations were averaged to give 479 symmetry independent reflections with only 4 unobserved ($F_o = 0$). Monitor reflections showed an intensity decrease of 1% at the end of 270 hours of X-ray exposure.

Absorption corrections for the spherical crystal were based on published tables (Weber, 1969). A^* values were interpolated for $\mu R = 3.38$ and $1/A^*$ was fitted to a 7th order polynomial in $\sin^2 \theta$. T values for extinction corrections (Zachariasen, 1968) were approximated by a similar 7th order polynomial. Both fits gave maximum errors of 0.5% or less in the range

Table 1. *Positional and thermal parameters for* $Tl_2PbCu(NO_2)_6$

The thermal parameters are of the form

$$T = \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	1.35 (2)					
Pb	0	0	$\frac{1}{2}$	1.47 (1)					
Tl	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2.95 (1)					
O	0.09922 (31)	0	0.25861 (31)	2.01 (12)	3.21 (15)	3.38 (16)	0	−0.38 (12)	0
N	0	0	0.19727 (53)	2.26 (19)	1.75 (17)	2.61 (22)			