Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 24.92°$
ω–2θ scans	$h = -10 \rightarrow 11$
Absorption correction: none	$k = 0 \rightarrow 11$
2771 measured reflections	$l = -10 \rightarrow 11$
2771 independent reflections	3 standard reflections
848 reflections with $I > 2\sigma(I)$	every 100 reflections
	intensity decay: 3%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.006$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$\Delta\rho_{max} = 0.194$ e Å^{-3}
$wR(F^2) = 0.104$	$\Delta\rho_{min} = -0.225$ e Å^{-3}
$S = 1.272$	Extinction correction: none
2771 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
202 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 2. *Selected geometric parameters (Å, °) for (3)*

O1—C8	1.221 (4)	N—C9	1.437 (4)
O2—C17	1.445 (4)	C1—C8	1.453 (5)
N—C8	1.387 (4)	C7—C16	1.336 (4)
N—C7	1.417 (4)	C16—C17	1.507 (4)
C8—N—C7	111.9 (3)	C7—C16—C17	139.7 (3)
N—C8—C1	106.5 (3)	O2—C17—C16	101.7 (3)
N—C7—C16—C17	−2.7 (8)	C7—C16—C17—O2	164.5 (5)
C9—N—C7—C16	7.4 (7)	C7—C16—C17—C19	48.2 (7)
C9—N—C8—O1	−6.2 (6)	C7—C16—C17—C18	−79.2 (6)

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structures: *MULTAN*88 (Debaerdemaeker *et al.*, 1988); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1225). Services for accessing these data are described at the back of the journal.

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2-*tert*-Butoxycarbonylamino-2-isopropyl-4-pentenamide, a new conformationally restricted α,α-dialkylglycine derivative†

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Abstract

The α-allyl-α-isopropylglycine derivative, $C_{13}H_{24}N_2O_3$, adopts a fully extended C_5 conformation. The φ and ψ torsion angles are close to the expected values of 180°. The amide C=O group plays the role of a double acceptor, namely, of an intramolecular hydrogen bond with the urethane N—H group, and of an intermolecular hydrogen bond with the amide N—H group of a symmetry-related molecule ($2 - x, -y, -z$).

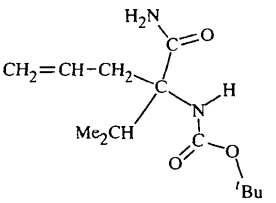
Comment

The incorporation of conformationally restricted residues, such as α,α-disubstituted amino acids, constitutes an important approach to studying the bioactive conformation of peptides, and also offers the potential to discover analogues with improved stability, bioselectivity and bioavailability. In this sense, α-allyl-substituted amino acids may not only be utilized to influence the local conformation of the peptide, but may also be used

† Alternative name: *tert*-butyl *N*-(1-aminocarbonyl-1-isopropylbut-3-enyl)carbamate.

as intermediates in the synthesis of complex amino acids and peptides (Holladay & Madzan, 1991; Bisang *et al.*, 1995; Zydowsky *et al.*, 1988).

In our laboratory, we have developed an efficient preparation of α,α-dialkyl amino acids based on the diastereoselective alkylation of α-cyanoesters with reactive alkyl halides (Cativiela *et al.*, 1995, 1997), and this method has recently been successfully applied to the synthesis of conveniently protected α-allyl-substituted amino acids (Badorrey *et al.*, 1997). As part of a programme aimed at establishing the conformational preferences of α,α-disubstituted glycyl residues (Buñuel *et al.*, 1997), we describe here the structural characterization of the title α-allyl amino acid derivative, (I).



(I)

A perspective view of a molecule of (I) is shown in Fig. 1. The compound is a racemate. It adopts an intermolecularly hydrogen-bonded fully extended C_5 conformation (Toniolo, 1980), as indicated by the following observations: the backbone torsion angles [C3—N2—C2—C1 (φ) 173.9 (3) and N2—C2—C1—N1 (ψ) −165.3 (2)°] are reasonably close to the expected values of 180°, and the intramolecular N2···O1 and N2—H2···O1 distances are 2.551 (3) and 1.98 Å. The N2—C2—C1 (τ) angle [103.1 (2)°] is remarkably compressed with respect to the tetrahedral value, as expected for a C_5 conformation (Toniolo & Benedetti, 1988). These data are in agreement with published data for other α,α-disubstituted glycines with long side chains (Valle *et al.*, 1990).

The spatial arrangement of the two side chains with respect to the peptide chain is defined by the torsion angles χ^{11} (N2—C2—C11—C12 and N2—C2—C11—C13) and χ^{12} (N2—C2—C8—C9) of 169.3 (3), −63.9 (3) and 51.7 (3)°, respectively. The urethane linkage is found in the usual *trans* conformation [O3—C3—N2—C2 (ω) 177.2 (2)°]. This, together with the *trans* arrangement of the C4—O3 bond relative to the C3—N2 bond [C4—O3—C3—N2 (θ) 159.3 (2)°], allows us to classify the urethane moiety as type *b* (*trans*, *trans*) (Benedetti *et al.*, 1980).

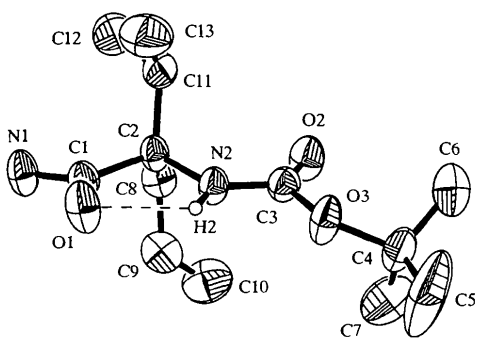


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids. All H atoms, except H2, which is involved in an intramolecular hydrogen bond, are omitted for clarity.

The crystal structure is stabilized by two intermolecular hydrogen bonds (N—H···O), involving two amide groups and the amide and the urethane groups, respectively [N1···O1^{i} 2.905 (3), N1···O2^{ii} 2.930 (3) Å; symmetry codes: (i) $2-x, -y, -z$; (ii) $\frac{5}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. The hydrogen-bonded molecules form infinite layers parallel to the crystallographic y axis.

Experimental

The compound was prepared according to the procedure previously described by Badorrey *et al.* (1997). Crystals were obtained by slow evaporation from a methanol solution.

Crystal data

$C_{13}H_{24}N_2O_3$
M_r = 256.34
Monoclinic
$P2_1/n$
a = 10.696 (5) Å
b = 11.305 (5) Å
c = 13.301 (5) Å
β = 110.060 (5)°
V = 1510.8 (11) Å^3
Z = 4
D_x = 1.127 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 41 reflections
θ = 4.57–12.5°
μ = 0.080 mm^{-1}
T = 293 (2) K
Prism
0.30 × 0.18 × 0.14 mm
Colourless

Data collection

Siemens $P4$ diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6067 measured reflections
2672 independent reflections
1548 reflections with $F > 4\sigma(F)$
R_{int} = 0.044

θ_{max} = 25°
$h = -1 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.054
$wR(F^2)$ = 0.154
S = 1.006
2672 reflections
165 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 0.2966P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ <0.001
$\Delta\rho_{max}$ = 0.154 e Å^{-3}
$\Delta\rho_{min}$ = −0.178 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.232 (3)	N2—C3	1.343 (3)
O2—C3	1.206 (3)	N2—C2	1.468 (3)
O3—C3	1.353 (3)	C1—C2	1.544 (3)
O3—C4	1.464 (3)	C2—C8	1.543 (4)
N1—C1	1.333 (3)	C2—C11	1.567 (4)
C3—O3—C4	121.8 (2)	C8—C2—C1	111.6 (2)
C3—N2—C2	127.2 (2)	N2—C2—C11	108.9 (2)
O1—C1—N1	121.1 (2)	C8—C2—C11	112.6 (2)
O1—C1—C2	120.3 (2)	C1—C2—C11	109.8 (2)
N1—C1—C2	118.6 (2)	O2—C3—N2	127.0 (2)
N2—C2—C8	110.4 (2)	O2—C3—O3	125.3 (2)
N2—C2—C1	103.15 (19)	N2—C3—O3	107.8 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.86	1.98	2.551 (3)	122.7
N1—H1*A*···O1^{i}	0.94	1.97	2.905 (3)	173.8
N1—H1*B*···O2^{ii}	0.85	2.21	2.930 (3)	142.1

Symmetry codes: (i) $2-x,-y,-z$; (ii) $\frac{5}{2}-x,y-\frac{1}{2},\frac{1}{2}-z$.

The structure was refined anisotropically by full-matrix least-squares methods. The H atoms at C5, C6 and C7 were fixed at ideal positions, and the other H atoms were located from a difference Fourier map. During the refinement, H atoms were allowed to ride on their parent atoms. Two 'free variables' were assigned, one to refine common isotropic displacement parameters for all methyl H atoms, and one for the rest of the H atoms. The high U_{eq} values of the *tert*-butyl group may indicate some rotational disorder. Software used for molecular geometry calculations: *PARST* (Nardelli, 1983).

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989). Software used to prepare material for publication: *SHELXL*93.

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2,5-Dichloro-1-(*p*-chlorobenzyl)-1*H*-benzimidazole

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Abstract

The crystal structure of the title compound, $C_{14}H_9Cl_3N_2$, is stabilized by C—H···Cl hydrogen bonds. All of the Cl atoms are involved in hydrogen bonding as acceptors.

Comment

Benzimidazole derivatives have provided a large number of biologically active compounds, and changing the substitution pattern on the benzimidazole moiety greatly alters the biological activity. For instance, amides and carbonates of 2-aminobenzimidazole have proved of considerable value as anthelmintic and antineoplastic agents, particularly in veterinary practice (Ram *et al.*, 1992). A series of benzimidazolone derivatives are useful for central nervous system disorders (Preston, 1974). Incorporation of a 4-aminopiperidine moiety onto the benzimidazole leads to a potent antihistamine, astemizole (Awouters *et al.*, 1983). Antibacterial and antifungal activities of the benzimidazoles have also attracted research interest (Kuş *et al.*, 1996). Gastric secretion inhibitors such as omeprazole and lansoprazole are extremely potent anti-ulcer drugs (Nishina *et al.*,