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A β-turn retro-enantiomeric analogue of achatin-I, H–D-Asp-[γCONH]-D-Ala–L-Phe–Gly–OH

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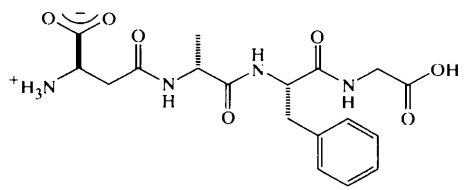
Abstract

A retro-enantiomeric analogue of achatin-I, β-D-aspartyl-D-alanyl-L-phenylalanylglycine, H–D-Asp-[γCO-NH]-D-Ala–L-Phe–Gly–OH ($C_{18}H_{24}N_4O_7$), was crystallized from an aqueous dimethylformamide solution. The γ-amide bond at the D-Asp[1] residue imparts β-amino acid characteristics on this residue. The peptide adopts a β-turn conformation and its loop shape is similar to that of achatin-I.

Comment

By reversing sequences using enantiomeric amino acids, we are using retro-enantiomeric (RE) methods to synthesize new peptides that mimic the conformation of the parent molecule (Doi *et al.*, 1995). This technique has now been applied to achatin-I (H–Gly–D-Phe–Ala–Asp–OH). Achatin-I was isolated from the ganglia of an African giant snail and is the first example of an endogenous neuropeptide having a D-amino acid (Kamatani *et al.*, 1989). The crystal structure determination of achatin-I has shown the molecule to have a β-turn conformation in the solid state (Kamatani *et al.*, 1990).

In the chemical syntheses of RE analogues of achatin-I, an additional approach was explored through the linkage of a γ-amide bond at the D-Asp[1] residue. RE-modified achatin-I (H–D-Asp–D-Ala–Phe–Gly–OH) and [γCONH]-RE-achatin-I (H–D-Asp-[γCONH]-D-Ala–Phe–Gly–OH; γ-REACH) were tested for crystallization and crystals of the latter peptide were obtained from an aqueous dimethylformamide solution.



γ-REACH

When the two carboxy groups are compared (D-Asp[1] and Gly[4]), the ionized states seem to be different. At the D-Asp[1] residue, the C1—O1 and C1—O1*T* bond distances are 1.242 (5) and 1.217 (5) Å, respectively, suggesting that the D-Asp[1] residue has an ionized carboxylate group and is a zwitterion. In contrast, significant differences are observed in the C4—O4 and C4—O4*T* bond lengths [1.211 (4) and 1.314 (4) Å, respectively] and the C-terminus of Gly[4] is assumed to be in the unionized carboxyl form.

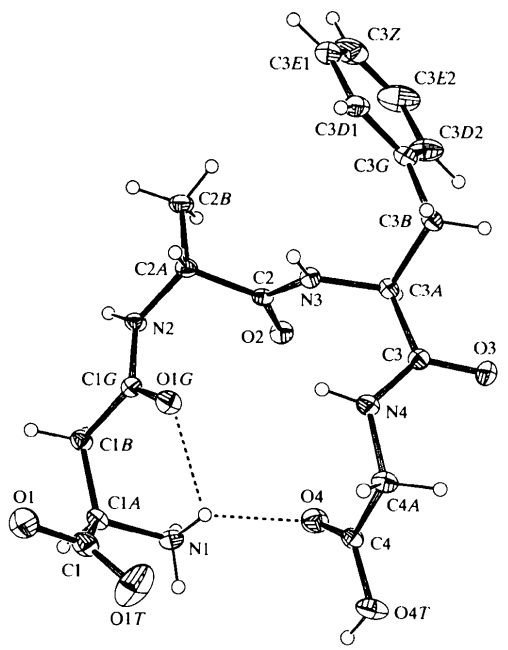


Fig. 1. A view of the title compound with displacement ellipsoids drawn at the 50% probability level.

The γ-REACH molecule adopts a β-turn conformation (Fig. 1). The turn is induced by an intramolecular hydrogen bond with an N1···O4 distance of 2.850 (4) Å (Table 1). Fig. 1 suggests the possibility of a typical β-turn hydrogen bond between atoms N4 and O1*G*, but the N4···O1*G* separation is 3.600 (4) Å. Atom O1*G* forms an intramolecular hydrogen bond with the N1 atom [3.104 (4) Å]. Consequently, a peptide loop is created by this intramolecular head-to-tail interaction. It seems that these hydrogen bonds co-operatively stabilize the β-like folded conformation. The structure and hydrogen bonding are similar to those of native achatin-I (Kamatani *et al.*, 1990). Superposition of the two structures leads to an r.m.s. deviation of 0.24 Å for the Cα atoms (Fig. 2). The spatial position of D-Asp[1] is slightly shifted from that of achatin-I and this is caused by the γ-linkage which imparts β-amino acid characteristics on this residue.

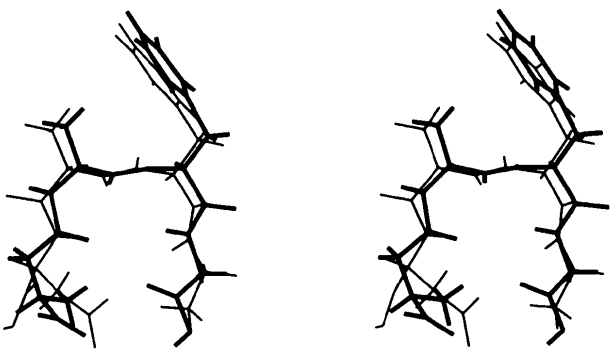


Fig. 2. A stereoview of the superimposed structures of γ-REACH (thick line) and native achatin-I (thin line).

Experimental

γ-REACH was synthesized by a conventional liquid-phase method using *tert*-butoxycarbonyl and benzyl ester protecting groups. The elongated peptide was purified by HPLC. No crystals were obtained from various aqueous alcohol solutions and crystals were finally obtained from an aqueous dimethylformamide solution.

Crystal data

$C_{18}H_{24}N_4O_7$
M_r = 408.41
Orthorhombic
$P2_12_12_1$
a = 16.517 (3) Å
b = 23.533 (5) Å
c = 5.1124 (6) Å
V = 1987.2 (6) Å^3
Z = 4
D_x = 1.365 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 19.78–20.16°
μ = 0.897 mm^{-1}
T = 293 (2) K
Needle
0.66 × 0.12 × 0.12 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$2\theta-\omega$ scans
Absorption correction: none
3910 measured reflections
1969 independent reflections (plus 1362 Friedel mates)
3107 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 64.61°
h = 0 → 19
k = −27 → 27
l = 0 → 5
4 standard reflections
every 100 reflections
intensity decay: −1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.143
S = 1.134
1969 reflections (plus 1362 Friedel mates)
266 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 2.3831P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.299 e Å^{-3}
$\Delta\rho_{min}$ = −0.298 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0148 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.1 (4)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1*G*	0.890	2.551	3.104 (4)	120.9
N1—H1*A*···O4	0.890	2.099	2.850 (4)	141.6
N3—H3···O2^{i}	0.860	2.125	2.958 (3)	163.2
N1—H1*B*···O1*G*^{ii}	0.890	2.045	2.933 (4)	175.8
N1—H1*C*···O1*T*^{iii}	0.891	1.876	2.744 (5)	164.4
O4*T*—H4*T*···O1^{iii}	0.820	1.717	2.485 (4)	155.3
N2—H2···O3^{iv}	0.860	2.065	2.890 (4)	160.4

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

Although determined with a relatively high s.u., refinement of the Flack (1983) parameter is consistent with the chirality expected from the known absolute stereochemistry of the starting materials. Scan widths were (1.470 + 0.3tanθ)° in ω, with a background/scan time ratio of 0.5. Intensities were measured to the mechanical limit of the diffractometer and included Friedel pairs. H atoms were calculated at idealized positions and refined with fixed isotropic displacement parameters (U_{iso} = 1.2U_{eq} of the associated C atom, or U_{iso} = 1.5U_{eq} for methyl C atoms).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1074). Services for accessing these data are described at the back of the journal.

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Bilayered structure of *N*,*N*′-diphenyl-4,4′-biphthalimide

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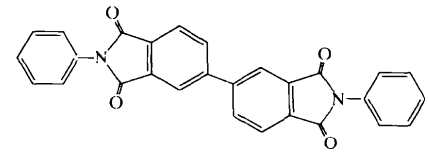
Abstract

The molecular and crystal structure of the title compound ($C_{28}H_{16}N_2O_4$), which corresponds to the monomer unit of the thermally stable polyimide, has been determined. The molecule is composed of a central phthalimide plane with phenyl ring planes at both ends twisted by 61.24 (8)°. The repeating unit along the *c* axis consists of a two-layer structure, in which the molecules tilt in opposite directions in adjacent layers.

Comment

Thermally stable polyimide, obtained by condensation polymerization of 3,3′,4,4′-biphenyltetracarboxylic dianhydride and bis(4-aminophenyl) ether, is one of the commercially available polymers that have several industrial applications. The title compound, (I), was synthesized using aniline instead of bis(4-aminophenyl) ether to investigate the stereochemistry and the physical properties of the chemical repeating unit of this polyimide.



(I)

Compound (I) has an inversion center in its chemical structure which coincides with the crystallographic inversion center. The molecule consists of a phthalimide plane at the center, with phenyl rings at both ends. The phthalimide plane, which is defined by N1, C7, C8, C9, C10, C11, C12, C13 and C14, has good planarity with a maximum deviation of 0.027 (2) Å. The phenyl ring plane is twisted from the phthalimide plane by 61.24 (8)°. The molecules are packed in a bilayered structure in which they tilt in opposite directions in adjacent layers. The carbonyl-O atoms have several short contacts with C atoms in adjacent molecules [O1···C6 3.234 (3) and O2···C10 3.299 (2) Å]. The distances between the O atoms and the H atoms attached to C6 and C10 are shorter than the van der Waals contacts, which suggests C—H···O hydrogen bonding.

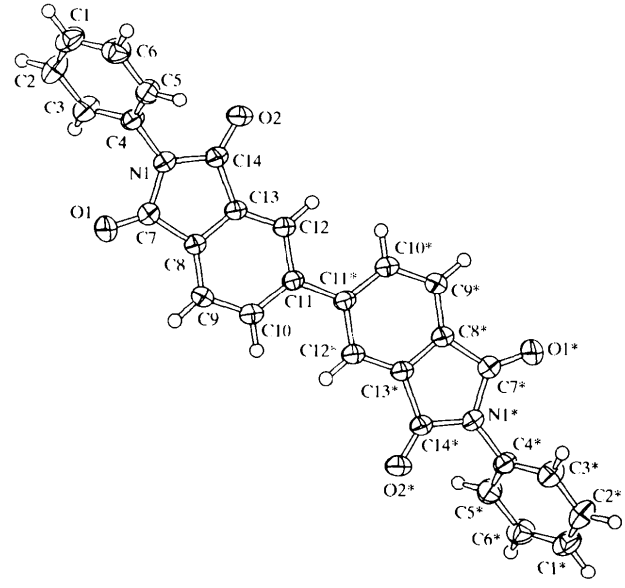


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title molecule with the atomic numbering scheme and non-H atoms represented by 50% probability displacement ellipsoids. Symmetrically generated atoms are denoted by *.

Experimental

The title compound was synthesized from 3,3′,4,4′-biphenyltetracarboxylic dianhydride and aniline. Single crystals used for X-ray diffraction were colorless and prismatic, and were obtained by the slow sublimation of a powdered sample in