2-Cyano-2-phenylsparteine

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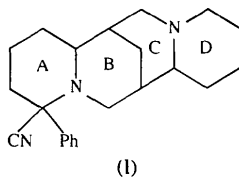
Abstract

Both quinolizidine moieties of [7S-(7α,7aα,14α,14aα)]-dodecahydro-4-methyl-7,14-methano-2H,6H-dipyrido-[1,2-a:1′,2′-e][1,5]diazocine-4-carbonitrile, $C_{22}H_{29}N_3$, have *trans* configurations, and the piperidine rings *A*, *B*, *C* and *D* assume chair, chair, boat and chair conformations, respectively. The phenyl substituent is in an equatorial orientation, while that of the cyano substituent is axial.

Comment

This work is a continuation of our studies on conformational dynamics of bisquinolizidine alkaloids. Sparteine has been used widely as a model compound for investigation of factors which cause conformational changes in the skeleton of the molecule. X-ray results for 2-cyano-2-phenylsparteine, (I), confirm our earlier observations that substituents at C2 do not alter the conformation of the sparteine skeleton (Katrusiak, Figas, Kałuski & Lesiewicz, 1989; Wolska & Borowiak, 1995). In 2-cyano-2-phenylsparteine the boat conformation of the *C* ring and the *trans* configuration of both quinolizidine systems are preserved. The *A/B* junction is *trans* [torsion angles C2—N1—C6—C5 −53.4 (4) and C7—C6—N1—C10 56.0 (4)°] and so too is the *C/D* junction [C9—C11—N16—C17 −52.0 (4) and C12—C11—N16—C15 61.1 (4)°]. The proper enantiomorph has been selected on the basis of the absolute configuration of naturally occurring sparteine derivatives (Klyne, Scopes, Thomas, Skolik, Gawroński & Wiewiórowski, 1974) to be C7-(*S*), C9-(*S*).

(I)

Rings *A*, *B* and *D* show almost no deviations from the ideal chair conformation. The largest distortions from the ideal form were found for the *C* ring, which adopts

a distorted boat conformation. Asymmetry parameters (Duax & Norton, 1975), which in this ring illustrate deviations from pseudo-mirror planes, are as high as $\Delta C_s^8 = 9.5°$ and $\Delta C_s^{9,11} = 9.8°$. The bond lengths and bond angles are similar to those found for other sparteine derivatives. The mean C_{sp^3}—C_{sp^3}, N1—C_{sp^3} and N16—C_{sp^3} bond lengths are 1.522 (4), 1.480 (5) and 1.464 (4) Å, respectively.
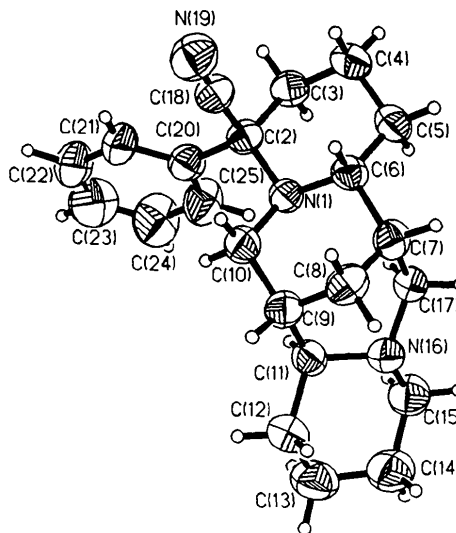

Fig. 1. View of the title compound, with displacement ellipsoids drawn at the 50% probability level.

The phenyl substituent occupies an equatorial position, which can be concluded from the values of torsion angles C4—C3—C2—C20 and C6—N1—C2—C20 of −178.1 (3) and 174.3 (3)°, respectively. The cyano group is axial with torsion angles C4—C3—C2—C18 63.9 (4) and C6—N1—C2—C18 −64.3 (4)°. Some strain introduced by the large phenyl substituent is evidenced by the asymmetry in the values of the valence angles characterizing inclination of one quinolizidine skeleton with respect to the other: C10—C9—C11 114.4 (3) and C6—C7—C17 111.9 (3)°. The equivalent values for 2-cyano-2-methylsparteine are 112.8 (2) and 113.0 (3)°, respectively (Wolska & Borowiak, 1995). In the crystal packing no significant short contacts have been observed.

Experimental

The title compound was crystallized from ethyl alcohol solution.

Crystal data

$C_{22}H_{29}N_3$	Cu *Kα* radiation
$M_r = 335.48$	$λ = 1.54178$ Å

Orthorhombic
$P2_12_12_1$
$a = 6.574\,(1)$ Å
$b = 16.083\,(3)$ Å
$c = 18.257\,(3)$ Å
$V = 1930.3\,(6)$ Å^3
$Z = 4$
$D_x = 1.154$ Mg m^{-3}

Cell parameters from 19
reflections
$\theta = 8.71–22.54°$
$\mu = 0.521$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.25 \times 0.2 \times 0.2$ mm
Colourless

Data collection

KM-4 four circle diffractom-
eter
$\omega/2\theta$ scans
Absorption correction:
none
1563 measured reflections
1563 independent reflections
1147 observed reflections
[$I > 2\sigma(I)$]

$\theta_{max} = 59.88°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 20$
2 standard reflections
monitored every 100
reflections
intensity decay: 3.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0470$
$wR(F^2) = 0.1229$
$S = 1.056$
1563 reflections
227 parameters
H-atom parameters not
refined
$w = 1/[\sigma^2(F_o^2) + (0.1086P)^2 + 0.1079P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.216$ e Å^{-3}
$\Delta\rho_{min} = -0.163$ e Å^{-3}

Extinction correction:
$F_c^* = kF_c[1 + (0.001\chi \times F_c^2\lambda^3/\sin2\theta)]^{-1/4}$
Extinction coefficient:
$\chi = 0.021\,(2)$
Atomic scattering factors
from *International Tables
for Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)
Absolute configuration:
Flack (1983) parameter
$-0.1\,(12)$

Table 1. *Fractional atomic coordinates and equivalent
isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.1356 (4)	0.1207 (2)	0.29394 (13)	0.0477 (7)
C2	0.1315 (5)	0.2102 (2)	0.2771 (2)	0.0508 (9)
C3	−0.0626 (6)	0.2327 (2)	0.2343 (2)	0.0574 (10)
C4	−0.0860 (7)	0.1820 (2)	0.1655 (2)	0.0613 (10)
C5	−0.0816 (7)	0.0902 (2)	0.1857 (2)	0.0607 (10)
C6	0.1074 (6)	0.0674 (2)	0.2281 (2)	0.0512 (9)
C7	0.1060 (6)	−0.0235 (2)	0.2522 (2)	0.0547 (9)
C8	0.3119 (6)	−0.0455 (2)	0.2846 (2)	0.0606 (10)
C9	0.3315 (6)	0.0055 (2)	0.3539 (2)	0.0584 (9)
C10	0.3222 (6)	0.0976 (2)	0.3343 (2)	0.0564 (10)
C11	0.1693 (6)	−0.0227 (2)	0.4103 (2)	0.0544 (9)
C12	0.2648 (7)	−0.0684 (3)	0.4744 (2)	0.0757 (12)
C13	0.1068 (8)	−0.0994 (3)	0.5285 (2)	0.0866 (14)
C14	−0.0558 (8)	−0.1489 (3)	0.4897 (2)	0.0825 (13)
C15	−0.1423 (7)	−0.1015 (3)	0.4257 (2)	0.0699 (11)
N16	0.0206 (5)	−0.0780 (2)	0.37501 (14)	0.0548 (8)
C17	−0.0634 (6)	−0.0411 (2)	0.3086 (2)	0.0537 (9)
C18	0.3072 (6)	0.2326 (2)	0.2290 (2)	0.0591 (10)
N19	0.4364 (6)	0.2479 (2)	0.1893 (2)	0.0794 (10)
C20	0.1396 (7)	0.2625 (2)	0.3474 (2)	0.0583 (10)
C21	0.2815 (8)	0.3243 (2)	0.3588 (2)	0.0752 (13)
C22	0.2704 (12)	0.3736 (3)	0.4209 (3)	0.100 (2)
C23	0.1238 (11)	0.3609 (3)	0.4720 (3)	0.105 (2)
C24	−0.0136 (10)	0.3008 (3)	0.4613 (3)	0.101 (2)
C25	−0.0081 (8)	0.2514 (3)	0.3998 (2)	0.0788 (13)

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

N1—C2	1.473 (4)	C11—N16	1.471 (5)
N1—C10	1.478 (5)	C11—C12	1.519 (5)
N1—C6	1.488 (4)	C12—C13	1.517 (6)
C2—C18	1.496 (5)	C13—C14	1.510 (6)
C2—C20	1.535 (5)	C14—C15	1.507 (5)
C2—C3	1.539 (5)	C15—N16	1.465 (5)
C3—C4	1.506 (5)	N16—C17	1.458 (4)
C4—C5	1.523 (5)	C18—N19	1.143 (5)
C5—C6	1.509 (5)	C20—C25	1.374 (6)
C6—C7	1.526 (5)	C20—C21	1.379 (6)
C7—C8	1.519 (5)	C21—C22	1.386 (6)
C7—C17	1.544 (5)	C22—C23	1.357 (8)
C8—C9	1.514 (5)	C23—C24	1.337 (8)
C9—C10	1.525 (5)	C24—C25	1.375 (6)
C9—C11	1.550 (5)		
C2—N1—C10	111.4 (3)	N1—C10—C9	113.2 (3)
C2—N1—C6	113.1 (2)	N16—C11—C12	108.6 (3)
C10—N1—C6	111.2 (3)	N16—C11—C9	110.1 (3)
N1—C2—C18	110.1 (3)	C12—C11—C9	111.7 (3)
N1—C2—C20	111.2 (3)	C13—C12—C11	112.2 (4)
C18—C2—C20	109.5 (3)	C14—C13—C12	110.7 (3)
N1—C2—C3	110.5 (3)	C15—C14—C13	111.3 (4)
C18—C2—C3	106.6 (3)	N16—C15—C14	110.1 (4)
C20—C2—C3	108.9 (3)	C17—N16—C15	110.7 (3)
C4—C3—C2	112.4 (3)	C17—N16—C11	111.7 (3)
C3—C4—C5	108.7 (3)	C15—N16—C11	111.4 (3)
C6—C5—C4	112.1 (3)	N16—C17—C7	110.9 (3)
N1—C6—C5	112.2 (3)	N19—C18—C2	176.6 (4)
N1—C6—C7	108.7 (2)	C25—C20—C21	117.8 (4)
C5—C6—C7	112.1 (3)	C25—C20—C2	119.1 (3)
C8—C7—C6	109.3 (3)	C21—C20—C2	122.9 (4)
C8—C7—C17	109.9 (3)	C20—C21—C22	119.9 (5)
C6—C7—C17	111.9 (3)	C23—C22—C21	121.0 (5)
C9—C8—C7	105.9 (3)	C24—C23—C22	119.2 (4)
C8—C9—C10	109.1 (3)	C23—C24—C25	121.2 (5)
C8—C9—C11	109.7 (3)	C20—C25—C24	120.8 (4)
C10—C9—C11	114.4 (3)		

Data collection: Kuma KM-4 diffractometer system (Kuma Diffraction, 1992). Cell refinement: Kuma KM-4 diffractometer system. Data reduction: Kuma KM-4 diffractometer system. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation* (Siemens, 1989). Software used to prepare material for publication: *SHELXL*93.

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molecule is in a folded conformation. The side-chain torsion angles χ_1, χ_2, χ_{31} and χ_{32} of the glutamine residue are 168.3 (2), 70.9 (3), −3.0 (3) and 177.2 (2)°, respectively. These values correspond to the lowest energy conformation of the glutamine side chain (Edsall *et al.*, 1966).

L-Glycyl-L-Glutamine Monohydrate†

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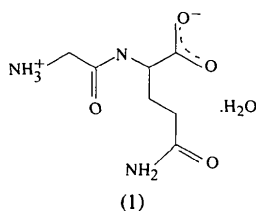
Abstract

The crystal structure of $C_7H_{13}N_3O_4.H_2O$ is stabilized by a three-dimensional network of N—H···O and O—H···O hydrogen bonds. The peptide unit exists in a *trans* conformation.

Comment

The investigation of the title compound (1) was undertaken as part of a project to determine the structures of peptides and other compounds containing the peptide linkage, to determine the conformation and crystal packing, and confirm the stereochemistry.
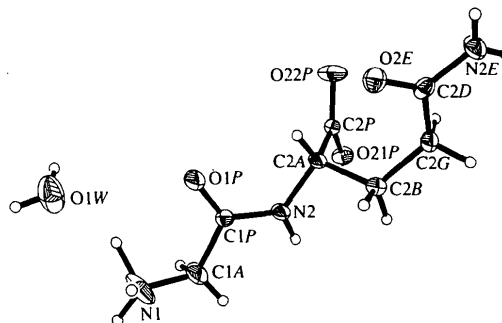

Fig. 1. The molecular structure of the title compound with the atom-labelling scheme and 50% probability displacement ellipsoids.

The molecular packing viewed down the a axis is shown in Fig. 2. The hydrogen-bonding scheme is given in Table 3. The NH_3^+ group of the glycyl residue is hydrogen bonded to $O1P$, symmetry-related $O1P$, $O21P$ and water oxygen ($O1W$). One of the H atoms (H1) is involved in bifurcated hydrogen bonds. The peptide N atom (N2) forms an N—H···O hydrogen bond of 2.943 (3) Å with a translated (a axis) $O22P$ atom. The water molecule ($O1W$) forms O—H···O hydrogen bonds with symmetry-related $O2E$ and
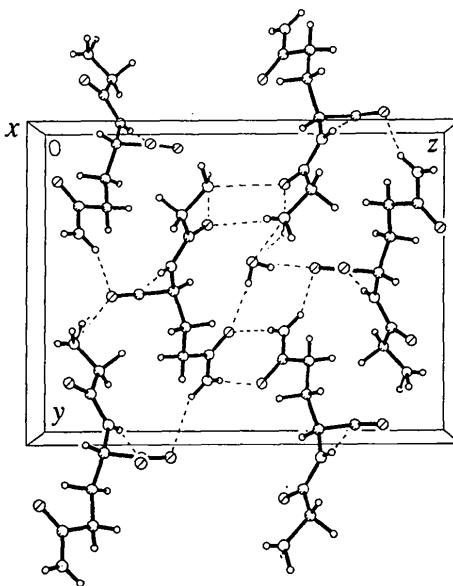
A view of the molecule with our numbering scheme is shown Fig. 1. The dimensions of the peptide group are in good agreement with the average values of peptide dimensions (Ramanadham & Chidambaram, 1978). The molecule exists as a zwitterion with the N atom (N1) of glycine protonated as NH_3^+ and the carboxyl group of the glutamine residue as ionized COO^-. The peptide unit is in a *trans* [$\omega = -179.6\,(2)°$] conformation and the peptide unit is planar within 0.002 (1) Å. The carboxyl group is also planar within 0.004 (1) Å and makes a dihedral angle of 57.5 (1)° with the adjacent peptide unit. The backbone torsion angles (Table 2) indicate the

Fig. 2. A perspective drawing of the packing arrangement (011) with dashed lines indicating the hydrogen-bonding scheme.