N11	0.2926 (2)	0.4115 (2)	0.7726 (2)	0.045
N13	0.3814 (1)	0.2622 (2)	0.7407 (2)	0.036
N17	0.1991 (1)	0.2612 (2)	0.5435 (2)	0.040
N19	0.3450 (1)	0.2552 (2)	0.5364 (2)	0.032
O12	0.4326 (2)	0.4020 (2)	0.8366 (2)	0.074
O14	0.3257 (1)	0.1137 (1)	0.6522 (2)	0.041
O15	0.1736 (1)	0.2072 (1)	0.7405 (2)	0.038
O16	0.1527 (2)	0.4212 (2)	0.7042 (3)	0.072
O18	0.2686 (1)	0.2770 (2)	0.3644 (2)	0.049
C21	0.0216 (2)	−0.0261 (2)	0.0390 (3)	0.056
C22	0.1231 (2)	0.1238 (2)	0.0444 (2)	0.041
C23	0.2287 (2)	0.2635 (4)	0.0526 (3)	0.063
C24	0.0817 (1)	0.2868 (2)	0.1419 (2)	0.033
C25	−0.0166 (1)	0.2561 (2)	0.1309 (2)	0.031
C26	−0.0318 (1)	0.1407 (2)	0.1064 (2)	0.035
C27	0.0530 (2)	0.4321 (3)	0.0182 (3)	0.054
C28	0.0208 (2)	0.2798 (2)	0.3247 (2)	0.038
C29	−0.0448 (2)	0.4158 (2)	0.0321 (3)	0.050
N21	0.0377 (2)	0.0838 (2)	0.0668 (2)	0.040
N23	0.1371 (1)	0.2267 (2)	0.0655 (2)	0.042
N27	−0.0478 (1)	0.2817 (2)	0.2470 (2)	0.038
N29	0.0977 (1)	0.2687 (2)	0.2644 (2)	0.037
O22	0.1796 (2)	0.0651 (2)	0.0070 (2)	0.061
O24	0.0957 (1)	0.3931 (2)	0.1211 (2)	0.046
O25	−0.0618 (1)	0.3061 (1)	0.0403 (2)	0.035
O26	−0.1037 (1)	0.1039 (2)	0.1241 (3)	0.056
O28	0.0154 (1)	0.2833 (2)	0.4318 (2)	0.049

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

C14—C15	1.552 (2)	C24—C25	1.550 (2)
C14—N13	1.441 (3)	C24—N23	1.440 (3)
C14—N19	1.442 (3)	C24—N29	1.445 (3)
C14—O14	1.404 (3)	C24—O24	1.406 (4)
C15—C16	1.519 (4)	C25—C26	1.531 (4)
C15—N17	1.455 (3)	C25—N27	1.451 (3)
C15—O15	1.392 (3)	C25—O25	1.402 (3)
N13—C14—N19	113.3 (2)	N23—C24—N29	114.0 (2)
N13—C14—O14	109.6 (2)	N23—C24—O24	109.4 (2)
N19—C14—O14	106.1 (2)	N29—C24—O24	107.3 (2)
N17—C15—O15	114.6 (2)	N27—C25—O25	114.6 (2)
C12—N13—C14—N19	82.5 (3)	C22—N23—C24—N29	76.7 (3)
C16—C15—C14—N13	32.0 (3)	C26—C25—C24—N23	34.3 (3)
C16—C15—C14—N19	−90.1 (2)	C26—C25—C24—N29	−87.8 (2)
C17—O14—C14—N19	−158.0 (2)	C27—O24—C24—N29	−158.3 (2)
N17—C15—C14—N19	28.4 (2)	N27—C25—C24—N29	29.7 (2)
O14—C14—C15—O15	38.6 (3)	O24—C24—C25—O25	38.7 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N17—H17···O28	0.992 (2)	2.117 (2)	3.083 (3)	164.1 (1)
N29—H29···O18	0.994 (2)	1.895 (2)	2.840 (3)	157.7 (1)
N19—H19···O28^{i}	0.980 (2)	2.012 (2)	2.895 (3)	148.8 (1)
N27—H27···O18^{ii}	0.992 (2)	2.357 (2)	3.187 (3)	140.7 (1)

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

Mean (Δ/σ) is 0.359. The relatively large displacement parameters for the *N*-methyl C11 atom can be attributed to slight disorder.

Data collection: Philips PW1100/20 software. Cell refinement: Philips PW1100/20 software. Data reduction: local program. Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *CSU* (Vicković, 1988, 1994).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and intra- and intermolecular contact distances, have been deposited with the IUCr (Reference: KA1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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DL-Glutamine

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Abstract

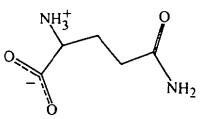
In the structure of DL-glutamine (3,5-diamino-5-oxopentanoic acid, $C_5H_{10}N_2O_3$), the molecules aggregate into double layers involving head-to-tail sequences stabilized by hydrogen bonds between main-chain atoms. The double layers are stacked along **a** with the help of hydrogen bonds between side-chain atoms. This pattern is fundamentally different from that in the structure of L-glutamine, but is very similar to those in the structures of DL-methionine and hydrated L-arginine D-glutamate. The essential features of different possible aggregation patterns of amino acids appear to be determined by interactions involving main-chain atoms.

Comment

Glutamine is among the very few amino acids for which the crystal structure of only the L isomer is known. We felt it important to determine the structure of the racemate for two reasons. Firstly, a comparison of the structures of L- and DL-amino acids provides useful insights into the effect of chirality on molecular aggregation (Soman & Vijayan, 1989). Secondly, our long-term program on the study of crystalline complexes involving amino acids and peptides (Vijayan, 1988; Prasad & Vijayan, 1993; Suresh, Prasad & Vijayan, 1994; Suresh & Vijayan, 1995), aimed at elucidating the geometrical features of biologically and evolutionary important interactions, involves the comparison of the

aggregation of L- and DL-amino acids with that in their crystalline complexes.

As in the structure of the L isomer (Cochran & Penfold, 1952; Koetzle, Frey, Lehmann & Hamilton, 1973), the side chain in DL-glutamine, (I), has a nearly planar extended conformation (Fig. 1, Table 2). The orientation of the side chain with respect to the main-chain atoms is, however, different in the two structures. The side chain is *trans* to the α-amino group in the racemate, whereas it is staggered between the α-amino and α-carboxylate groups in the L isomer.



(I)

Amino acid molecules usually aggregate into layers or double layers, which then stack to form the crystal. In most cases, the aggregation pattern in the structure of the L-amino acid and that in the corresponding DL-amino acid remains essentially the same, the effects of the change in chirality of half the molecules being accommodated through comparatively small structural adjustments (Soman & Vijayan, 1989). Glutamine is among the few amino acids which aggregate very differently in the crystals of the L isomer and the racemate. As in the crystal structures of most other hydrophilic L-amino acids, that of L-glutamine is made up of layers involving *S*2 and *Z*2 head-to-tail sequences (Suresh & Vijayan, 1983) (an *S*2 sequence is produced by translationally related amino acid molecules being connected by N1—H···O2 hydrogen bonds, while a *Z*2 sequence involves screw-related molecules connected by the same type of hydrogen bonds). The molecules in the structure of DL-glutamine (Fig. 2, Table 3), on the other hand, aggregate into double layers stacked along **a**. Each layer in the double layer involves a pair of *DL*2 head-to-tail sequences (a *DL*2 sequence contains glide-related molecules connected by N1—H···O2 hydrogen bonds). The interaction between the two layers involves a *Z*1-type head-to-tail sequence (in which the O1 atom is the hydrogen-bond acceptor instead of O2 as in the *Z*2-type sequence). The double layers are interconnected through side chain–side chain hydrogen bonds. An interesting feature of the interface between the double layers is the occurrence of a specific interaction, involving two parallel hydrogen bonds, between the amide groups of the two side chains which face each other. This interaction is geometrically similar to the Type A specific interaction involving the guanidyl group (Salunke & Vijayan, 1981; Vijayan, 1988).

Surprisingly, the aggregation of molecules in the crystals of DL-glutamine is almost identical to that in one crystal form of DL-methionine (Mathieson, 1952). The only significant difference is in the nature of the side chain–side chain interactions. The space group and unit-cell dimensions (α-DL-methionine: $P2_1/a$, a = 9.76, b = 4.70, c = 16.70 Å, β = 102°) of the two structures also reflect this close relationship. The aggregation of molecules in β-DL-methionine is also similar, though the unit cell contains two double layers with an appropriate doubling of one of the cell dimensions (β-DL-methionine: $I2/a$, a = 9.94, b = 4.70, c = 33.40 Å, β =

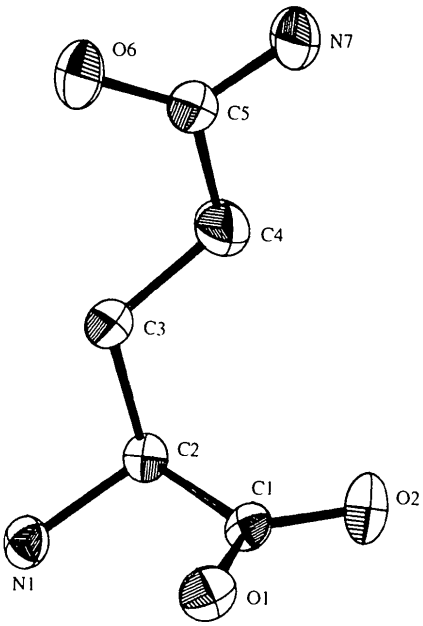


Fig. 1. A perspective view of the title molecule showing the atom-labelling scheme. Ellipsoids are at the 50% probability level.

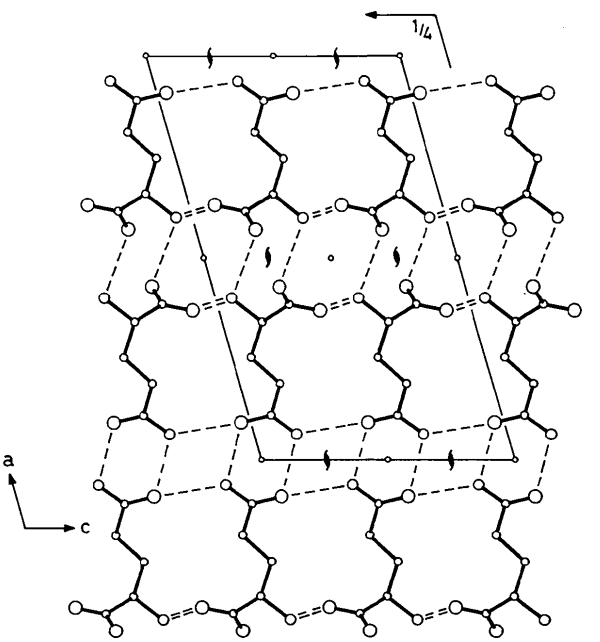


Fig. 2. The crystal structure of the title compound as viewed along the *b* axis. C, N and O atoms are represented by spheres of increasing size.

106.6°). Interestingly, a very similar aggregation pattern is observed in the crystalline complexes L-arginine D-glutamate monohydrate (Soman & Vijayan, 1989) and L-arginine D-glutamate trihydrate (Suresh, Ramaswamy & Vijayan, 1986). Each layer in the double layer in the complexes is made up of an equal number of L-arginine and D-glutamate ions. Both complexes are in space group $P2_1$, but the main-chain atoms and some side-chain atoms obey a $P2_1/a$ pseudosymmetry. The unit-cell dimensions are also comparable with those of α-DL-methionine (and DL-glutamine after interchanging the a and c axes). The longest unit-cell edge is larger in the complexes on account of the presence of water molecules in the interfaces between double layers. The fact that DL-methionine (a hydrophobic amino acid), DL-glutamine (a hydrophilic amino acid) and hydrated L-arginine D-glutamate (a complex between basic and acidic amino acids) exhibit the same pattern of aggregation, suggests that the basic features of different possible amino acid aggregation patterns are determined by interactions involving main-chain atoms, although the choice of pattern may be dictated by the side chains.

Experimental

The title compound was obtained commercially from the Sigma Chemical Company. The crystals used for analysis were grown from aqueous solution by slow evaporation.

Crystal data

$C_5H_{10}N_2O_3$
M_r = 146.15
Monoclinic
$P2_1/c$
a = 16.051 (2) Å
b = 4.6538 (10) Å
c = 9.9373 (12) Å
β = 106.484 (9)°
V = 711.8 (2) Å^3
Z = 4
D_x = 1.364 Mg m^{-3}
D_m = 1.36 (2) Mg m^{-3}
D_m measured by flotation in C_6H_6–CCl_4
Mo $K\alpha$ radiation
λ = 0.71068 Å
Cell parameters from 25 reflections
θ = 7.1–20.2°
μ = 0.113 mm^{-1}
T = 296 (2) K
Plate
0.50 × 0.30 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
1590 measured reflections
1538 independent reflections
1200 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.023
θ_{max} = 27°
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 5$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 6.3%

Refinement

Refinement on F^2
$R(F)$ = 0.0406
$wR(F^2)$ = 0.1304
S = 1.108
1538 reflections
131 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0837P)^2 + 0.0594P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.054$
$\Delta\rho_{max}$ = 0.269 e Å^{-3}
$\Delta\rho_{min}$ = −0.231 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
O1	0.43005 (7)	0.6657 (2)	0.76559 (12)	0.0310 (3)
O2	0.37068 (8)	0.9368 (3)	0.89848 (11)	0.0352 (3)
N1	0.40154 (9)	1.0692 (3)	0.56461 (13)	0.0253 (3)
C1	0.38603 (9)	0.8739 (3)	0.78498 (14)	0.0222 (3)
C2	0.34318 (9)	1.0612 (3)	0.65735 (14)	0.0220 (3)
C3	0.25512 (10)	0.9388 (4)	0.5748 (2)	0.0295 (4)
C4	0.18943 (12)	0.9269 (5)	0.6583 (2)	0.0440 (5)
C5	0.11087 (10)	0.7489 (5)	0.5877 (2)	0.0392 (4)
O6	0.09268 (9)	0.6846 (5)	0.46235 (13)	0.0636 (5)
N7	0.06329 (12)	0.6613 (5)	0.6689 (2)	0.0559 (6)

Table 2. *Selected torsion angles (°)*

O1—C1—C2—N1 (ψ^1)	−33.8 (2)	C3—C4—C5—O6 (χ^{31})	−17.2 (3)
N1—C2—C3—C4 (χ_1^1)	−178.7 (2)	C3—C4—C5—N7 (χ^{32})	161.7 (2)
C2 C3 C4 C5 (χ^2)	−167.5 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···O1^i	2.787 (2)	1.88 (2)	3 (2)	176 (2)
N1—H2N1···O2^{ii}	2.791 (2)	1.89 (2)	8 (2)	168 (2)
N1—H3N1···O2^{iii}	2.838 (2)	1.95 (2)	8 (2)	169 (2)
N7—H1N7···O6^{iv}	2.909 (2)	2.07 (3)	7 (2)	170 (3)
N7—H2N7···O6^v	2.951 (3)	2.02 (3)	3 (2)	176 (3)

Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $x, \frac{5}{2}-y, z-\frac{1}{2}$; (iii) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (v) $-x, 1-y, 1-z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) for Fig. 1 and *PLUTO* (Motherwell & Clegg, 1978) for Fig. 2.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1304). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2*R*,5*S*)-2,3-Diphenyl-1,3,2-diazaphospha-bicyclo[3.3.0]octane–Borane

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Abstract

The title complex, $C_{17}H_{22}BN_2P$, (3), is one of a series of new chiral diazaphospholidine–borane complexes used as catalysts in the enantioselective borane reduction of ketones. We describe herein the determination of the molecular structure of (3) and the absolute configuration about the P atom.

Comment

Recently, we reported a new method for the enantioselective reduction of ketones with BH_3:THF, catalyzed by a chiral tricoordinated phosphorus–borane complex (Brunel, Pardigon, Faure & Buono, 1992; Buono, Brunel, Faure & Pardigon, 1993). The study of the title compound, (3), was undertaken in order to probe the mechanism of the reduction and to establish the absolute configuration about the P atom. Complex (3) was synthesized by reaction of bis(dimethylamino)phenylphosphine, (1), with (*S*)-(+)-2-anilinomethylpyrrolidine, (2), in refluxing toluene and complexation by one equivalent of BH_3:THF.

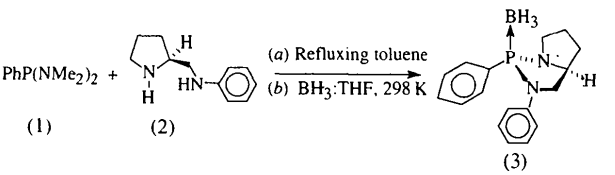

Fig. 1 is a view of the title molecule showing the numbering of the atoms (*PLUTO*; Motherwell & Clegg, 1978).

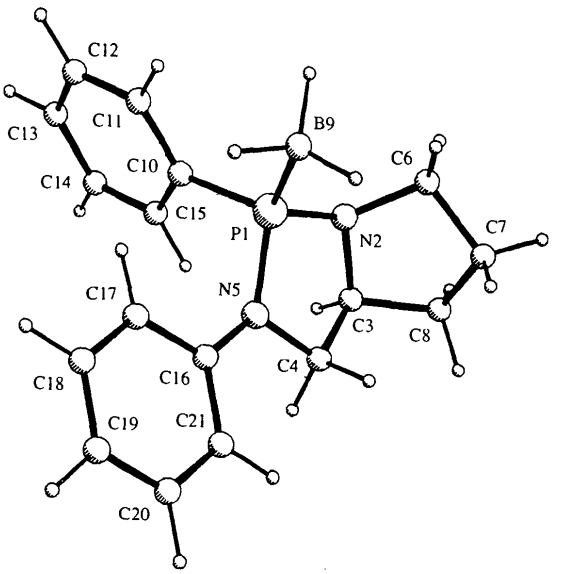

Fig. 1. View of the title compound (*PLUTO*; Motherwell & Clegg, 1978) showing the atom-labelling scheme.

Experimental

Crystal data

$C_{17}H_{22}BN_2P$
M_r = 296.16
Orthorhombic
$P2_12_12_1$
a = 10.197 (2) Å
b = 9.086 (2) Å
c = 17.807 (5) Å
V = 1649.8 (6) Å^3
Z = 4
D_x = 1.19 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 30 reflections
θ = 15–35°
μ = 1.402 mm^{-1}
T = 291 K
Parallelepiped
0.60 × 0.60 × 0.50 mm
White