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2-(2,3-Diphenylpiperazin-1-yl)ethylammonium chloride

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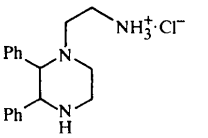
Abstract

In the title compound ($C_{18}H_{24}N_3^+ \cdot Cl^-$), the hydrochloride of a substituted piperazine, the amino-N atom is protonated. The conformation at the ethyl-C atoms is *gauche*, with the two phenyl groups approximately orthogonal to the piperazine ring. The crystal structure is stabilized by hydrogen bonds involving the chloride ion and the protonated N atom.

Comment

Piperazine and its derivatives form an important class of organic compounds with versatile chelating ability (Marzotto *et al.*, 1998) and pharmacological applications (Liu *et al.*, 1998). Some metal complexes of piperazine are also known for their antitumoural activity (Ciccarese *et al.*, 1998). During our ongoing programme of the synthesis and reactivity of imidazo[1,2-*a*]pyrazines, the title compound, (1), a hydrochloric acid salt of a diphenylpiperazine derivative, was obtained. The crystal structure determination of (1) was undertaken to elucidate the molecular conformation.



(1)

The bond lengths and angles in (1) are comparable to those observed in related piperazine derivatives (Parihar *et al.*, 1995; Thirumurugan *et al.*, 1998; Tyrselova *et al.*, 1995; Okamoto *et al.*, 1992). The torsion angle C1—C7—C12—C13 is 58.6 (3)°, corresponding to a *gauche* conformation at C7—C12. The piperazine ring adopts a chair conformation with the N1 and N2 atoms deviating by 0.743 (3) and 0.585 (3) Å, respectively, on opposite sides of the least-squares plane through C7, C8, C9 and C12 [maximum deviation of an in-plane atom 0.016 (4) Å]. The two phenyl rings (C1–C6 and C13–C18) are inclined at 37.8 (1)° to each other and at angles of 97.8 (2) and 95.3 (2)° to the piperazine ring. The amino-N atom (N3) is protonated. The crystal packing is stabilized by a network of hydrogen bonds (Table 2) involving the chloride ion and the protonated N (N3) atom.

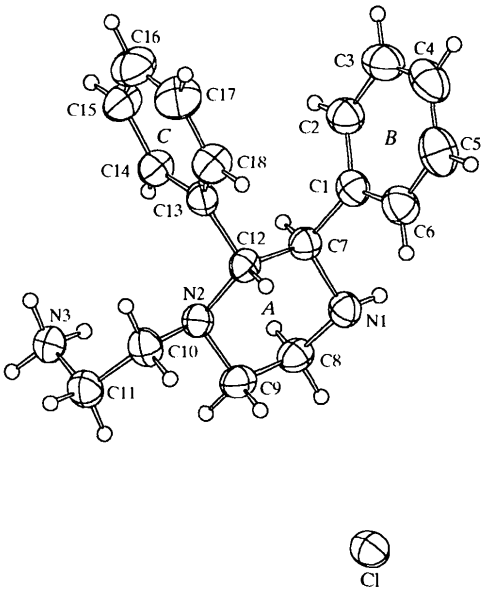


Fig. 1. A *ZORTEP* (Zsolnai, 1995) view of (1) showing 50% probability displacement ellipsoids for the non-H atoms. H atoms are shown as circles of an arbitrary radius.

Experimental

8,8a-Diphenyl-1,2,3,5,6,8a-hexahydroimidazo[1,2-*a*]pyrazine (DPHP) was prepared by adding diethylenetriamine (50 mmol) dropwise to a methanolic solution of benzil (50 mmol) with constant stirring followed by refluxing for 4 h in a dry atmosphere. $NaBH_4$ (66 mmol) was added pinchwise with constant stirring for 6 h to a solution of DPHP (18 mmol) dissolved in 175 mml of methanol–water (6:1) mixture. The reaction mixture was extracted with 50 ml of benzene. Removal of excess solvent yielded 2-(2,3-diphenylpiperazin-1-yl)ethylammonium monohydrate, (2). Single crystals of (1) suitable for X-ray studies were obtained by direct diffusion of hexane into a dichloromethane solution of (2).

Crystal data

$C_{18}H_{24}N_3^+ \cdot Cl^-$
$M_r = 317.85$
Orthorhombic
Pbca
$a = 13.585\ (2)$ Å
$b = 35.391\ (7)$ Å
$c = 7.067\ (2)$ Å
$V = 3398\ (1)$ Å^3
$Z = 8$
$D_x = 1.243$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 14$–$20°$
$\mu = 1.976$ mm^{-1}
$T = 296.2$ K
Prism
0.25 × 0.25 × 0.15 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{min} = 0.634$, $T_{max} = 0.743$
3378 measured reflections
3378 independent reflections
2176 reflections with $I > 2\sigma(I)$
$\theta_{max} = 79.40°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 45$
$l = 0 \rightarrow 8$
3 standard reflections
every 150 reflections
intensity decay: < 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.137$
$S = 1.042$
3344 reflections
221 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 4.0173P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.028$
$\Delta\rho_{max} = 0.252$ e Å^{-3}
$\Delta\rho_{min} = -0.273$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C8	1.462 (4)	C1—C7	1.511 (5)
N1—C7	1.466 (4)	C7—C12	1.540 (5)
N2—C10	1.462 (5)	C8—C9	1.499 (5)
N2—C9	1.470 (4)	C10—C11	1.513 (5)
N2—C12	1.475 (4)	C12—C13	1.511 (4)
N3—C11	1.486 (5)		
C8—N1—C7	107.5 (3)	N1—C8—C9	108.4 (3)
C10—N2—C9	110.8 (3)	N2—C9—C8	111.8 (3)
C10—N2—C12	110.7 (3)	N2—C10—C11	112.0 (3)
C9—N2—C12	112.3 (2)	N3—C11—C10	110.8 (3)
N1—C7—C1	112.4 (3)	N2—C12—C13	110.3 (3)
N1—C7—C12	109.2 (3)	N2—C12—C7	111.0 (3)
C1—C7—C12	110.4 (3)	C13—C12—C7	108.6 (3)
C8—N1—C7—C12	64.5 (3)	N2—C10—C11—N3	−55.1 (4)
C7—N1—C8—C9	−66.4 (3)	C9—N2—C12—C7	49.0 (3)
C12—N2—C9—C8	−51.6 (4)	N1—C7—C12—N2	−55.9 (3)
N1—C8—C9—N2	60.1 (4)	C1—C7—C12—C13	58.6 (3)

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

D—H···*A*	*D*···H	*D*···*A*	*D*—H···*A*
N3—H3*C*···N1^{i}	0.96	2.985 (4)	126.8
N3—H3*A*···Cl^{i}	0.96	3.117 (3)	142.5
N3—H3*B*···Cl^{ii}	0.96	3.249 (3)	144.5
N1—H1···Cl^{iii}	0.86	3.380 (3)	144.9

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

The displacement factors of all H atoms were refined isotropically (the positions were kept fixed).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *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: HA1247). Services for accessing these data are described at the back of the journal.

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L-Leucyl-L-leucine 2-methyl-1-propanol solvate

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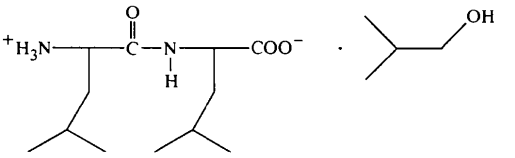
Abstract

The title compound, $C_{12}H_{24}N_2O_3 \cdot C_4H_{10}O$, crystallizes in space group $P2_12_12_1$ with two peptide molecules and two alcohol molecules in the asymmetric unit. The structure has been studied as part of a systematic survey of solvent inclusion for the L-Leu-L-Leu dipeptide, which has previously been crystallized as isomorphous ethanol, 1-propanol and 2-propanol solvates, and also as a dimethyl sulfoxide solvate.

Comment

Dipeptides with two hydrophobic residues (hydrophobic dipeptides) generally crystallize as needles, or occasionally as thin plates. L-Leu-L-Val, on the other hand, forms good quality large crystals in vapour-diffusion experiments with most solvents as precipitating agents, either as a hydrate in a hexagonal space group (Görbitz & Gundersen, 1996*a*) or as an alcohol solvate (Görbitz & Torgersen, 1999). L-Leu-L-Leu can also form good quality crystals, but for this compound, the outcome of crystallization is much more dependent on the choice of solvent. The structure of the dimethyl sulfoxide (DMSO) solvate has been reported previously (space group $P2_1$, $Z = 2$; Mitra & Subramanian, 1994); the 'ill-formed crystals' were obtained 'after a great deal of effort' as extremely thin needles. A survey of numerous other solvents (Görbitz, 1999) revealed that only four produced crystals suitable for diffraction experiments. Three of these, ethanol, 1-propanol and 2-propanol, form isomorphous structures in space group $P2_1$ with $Z = 4$ (Görbitz, 1999*a*). The fourth is 2-methyl-1-propanol (isobutanol), which forms the title complex, LLmp. The use of other solvents during crystallization produces exceedingly thin needles (< 0.01 mm diameter), as does slow cooling of an aqueous solution. We anticipate that the structure of L-Leu-L-Leu in needles devoid of organic solvent is related to the hexagonal structures observed for other hydrophobic dipeptides (Görbitz & Gundersen, 1996*b*; Görbitz, 1999).



LLmp

The asymmetric unit of the L-Leu-L-Leu 2-methyl-1-propanol solvate (LLmp), with two peptide molecules and two alcohol molecules, is depicted in Fig. 1. Bond lengths and angles are normal. The main chains of both peptide molecules are in fairy extended conformations. The side chain of the N-terminal residue of molecule *A* has the common *gauche*$^-$/*trans*,*gauche*$^-$ conformation for $\chi^1/\chi^{2,1},\chi^{2,2}$, while for residue 2, the conformation is *trans*/*trans*,*gauche*$^+$. The side chains of the two residues in molecule *B* have the same two conformations, but in opposite order. There is a significant deviation from planarity for the peptide bond of molecule *B*, easily visible in Fig. 1, with $\omega = 168.4\,(2)°$.

As in numerous other dipeptides, the crystal structure of LLmp is divided into hydrophilic and hydrophobic

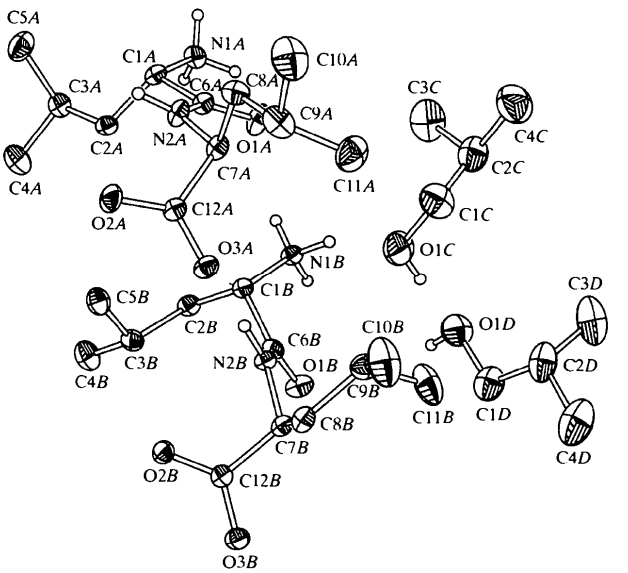


Fig. 1. The asymmetric unit of LLmp with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level and selected H atoms are shown as spheres of arbitrary size.