The title salt crystallized in the monoclinic system. Precession and Weissenberg photographs indicated a high degree of pseudo-C-centering. The structure was finally solved in space group $P2_1/c$. Attempts to solve and refine the structure in $C2/c$ led to an R factor of 26%. The S atom of the sulfate ion sits on the pseudo-twofold axes generated by the non-crystallographic C-centering. The phenyl C atoms for both the molecules in the asymmetric unit were regularized with C—C bond lengths of 1.39 Å. The phenyl rings were refined as rigid groups until the last few cycles of refinement. Due to very high correlation between the two molecules of the asymmetric unit, it was difficult to achieve convergence in the refinement and so damping was used during refinement. All the H atoms, except those of the water molecule, were placed in geometrically calculated positions, with an average C—H distance of 0.953 Å and an average N—H distance of 0.90 Å. They were included in the refinement but were restrained to ride on their parent atoms. The isotropic displacement parameters of the H atoms were held fixed to $1.2U_{eq}$ of their riding atoms. The H atoms of the water molecules were located from difference Fourier maps and kept completely fixed. All hydrogen-bond calculations were carried out using *PARST* (Nardelli, 1983).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*2.1a (McArdle, 1993). Software used to prepare material for publication: *SHELXL*93.

The authors acknowledge the National Diffractometer Facility (DST) at the Department of Biophysics, AIIMS, New Delhi, for intensity data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1069). Services for accessing these data are described at the back of the journal.

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D-Phenylglycine Hydrochloride

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Abstract

In the title compound, $C_8H_{10}NO_2^+.Cl^-$, the hydrochloride of a ring-substituted amino acid, the amino N atom is protonated. As in other amino acids, this atom lies nearly in the plane of the carboxyl group, indicating thereby that the orientation of the group is unaffected by the phenyl substitution at the α-C atom. The crystal structure, consisting of alternating layers of hydrophobic and hydrophillic zones, is stabilized by hydrogen bonds involving mostly the Cl atom.

Comment

D-Phenylglycine is an important starting material in the production of β-lactams such as semisynthetic penicillins and cephalosporins. Many phenylglycine derivatives are also well known for their use in the synthesis of antitumor drugs and other pharmacological applications (Satyam *et al.*, 1996, Jayasinghe *et al.*, 1994).

The amino N atom in the title molecule, (I), is protonated. The bond lengths and angles in the structure compare well with those found in α-glycine (Marsh, 1958), diglycine hydrochloride (Hahn & Buerger, 1957; Faamau & Tiekink, 1993), the crown ether inclusion complex of (R)-phenylglycine methyl ester (Goldberg, 1977) and (R)-($-$)-1-phenylglycinium hydrogen squarate monohydrate (Angelova *et al.*, 1996). The torsion angle N—C7—C8—O1, which indicates the relative orientation of the carboxyl group and the amino N atom, is 18.9 (5)°. This value is close to the corresponding values of 19.1 and 16.3° in α-glycine (Marsh, 1958) and diglycine hydrochloride (Hahn & Buerger, 1957; Faamau & Tiekink, 1993), respectively, thereby indicating that the orientation of the carboxyl group is not influenced by the phenyl substitution at the α-C atom. The orientation of the phenyl ring, as described by the torsion angle C3—C4—C7—N of 129.2 (3)°, is close to the corresponding value (137.6°) in (R)-phenylglycine methyl ester (Goldberg, 1977) and that (119.9°) in (R)-($-$)-1-phenylglycinium hydrogen squarate monohydrate (Angelova *et al.*, 1996).

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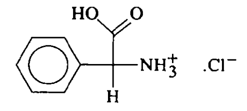

(I)

The hydrogen-bonding parameters that stabilize the crystal structure are listed in Table 1. There are four H atoms available for hydrogen-bond formation, three from the NH_3^+ group and one from the carboxylic OH group. All of them participate in hydrogen bonds with Cl^-. In addition, there is a weak $N^+—H\cdots O$ hydrogen bond involving O1, the double-bonded O atom of the carboxylic group, as in other similar compounds referred to earlier. As in most crystal structures of amino acids with non-polar side chains, the aggregation of the molecule involves alternating hydrophillic and hydrophobic zones.

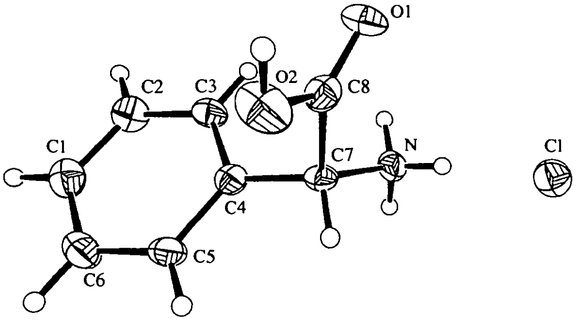

Fig. 1. *ORTEX* (McArdle, 1993) view of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 40% probability level. H atoms are drawn as small circles of arbitrary radii.

Experimental

D-Phenylglycine was obtained commercially from the Sigma Chemical Company and the crystals were obtained by slow evaporation of its solution in dilute HCl.

Crystal data

$C_8H_{10}NO_2^+.Cl^-$
$M_r = 187.625$
Orthorhombic
$P2_12_12_1$
$a = 5.4376\,(5)$ Å
$b = 7.2577\,(8)$ Å
$c = 22.773\,(2)$ Å
$V = 898.72\,(15)$ Å^3
$Z = 4$
$D_x = 1.387$ Mg m^{-3}
$D_m = 1.365$ Mg m^{-3}
D_m measured by flotation in benzene–bromoform

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3$–$25°$
$\mu = 0.383$ mm^{-1}
$T = 293\,(2)$ K
Needle-shaped
0.45 × 0.30 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{min} = 0.784$, $T_{max} = 0.909$
964 measured reflections
964 independent reflections

853 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 27$
3 standard reflections every 200 reflections intensity decay: not significant

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.106$
$S = 0.747$
961 reflections
110 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1109P)^2 + 0.8971P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.255$ e Å^{-3}
$\Delta\rho_{min} = -0.277$ e Å^{-3}

Extinction correction: *SHELXL*93
Extinction coefficient: 0.027 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (16)

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

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N—H9···Cl	2.41	3.230 (3)	152
O2—H4···Cl^{i}	2.23	3.051 (3)	172
N—H8···Cl^{ii}	2.33	3.216 (3)	168
N—H10···Cl^{iii}	2.45	3.321 (3)	165
N—H9···O1^{iii}	2.60	3.053 (4)	111

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

All the H atoms could be located from a difference Fourier map, except that of the carboxylic group, which was fixed geometrically. They were treated as riding on the heavier atoms to which they are attached. Hydrogen-bonding calculations were performed using *PARST* (Nardelli, 1995).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*2.1a (McArdle, 1993) . Software used to prepare material for publication: *SHELXL*93.

The authors acknowledge the help of the Regional Sophisticated Instrumentation Centre (DST) at the Bose Institute, Calcutta, for intensity data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1074). Services for accessing these data are described at the back of the journal.

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A Low-Temperature Phase of 2-Pyrrolidone

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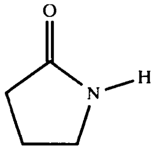
Abstract

Differential scanning calorimetry in the range 173–303 K reveals the presence of a previously unknown metastable phase of 2-pyrrolidone, C_4H_7NO, with a melting point of 286 K. Its crystal structure at 173 K is described. The molecules crystallize as centrosymmetric dimers and are linked by N—H···O hydrogen bonds with each molecule adopting an unstrained envelope conformation. Theoretical calculations confirm a slight pyramidalization of the N atom.

Comment

The report by Kondepudi *et al.* (1990) that cooling a vigorously stirred saturated aqueous solution of sodium chlorate ($NaClO_3$) results in a predominance of enantiomorphic crystals of one handedness highlights the possibility of obtaining chiral crystals in high yield from a solution of an achiral species. It appears that nucleation plays a decisive role in determining the outcome of the experiment (McBride & Carter, 1991). We have recently begun a search for organic systems that behave similarly. Our starting point was the observation that planar tetrazole can be made to crystallize as a conglomerate (Goddard *et al.*, 1997*a*). Interestingly, none of the other known isoelectronic aza derivatives of pyrrole resulting from progressive substitution of C—H by N exhibits this property (Goddard *et al.*, 1997*b*). Nevertheless, encouraged by the observation that the achiral molecule acetamide crystallizes in a non-centrosymmetric (Senti & Harker, 1940; Denne & Small, 1971; Jeffrey *et al.*, 1980) as well as a centrosymmetric space group (Hamilton, 1965), we decided to investigate the crystallization of pyrrolidone (2-pyrrolidone), (I).



(I)

While studying the thermal behaviour of (I) in the range 243–313 K by differential scanning calorimetry (DSC), we were intrigued to observe on heating that, prior to an endothermic transition at 293 K, there was an endothermic heat flow at 286 K, accounting for 13% of the energy absorbed. Cooling the sample to 173 K resulted in a reproducible retention of the endothermic transition at 286 K and disappearance of the endothermic transition at 293 K, even though the sample was heated to 303 K during each cycle (Fig. 1, top). Subsequently, we restricted the temperature range to 253–303 K and observed the gradual re-emergence of a small shoulder on the higher temperature side of the 286 K endothermic peak, but reversion to the original endothermic transition at 293 K did not occur. However, when a fresh sample was cooled to just 253 K, the endothermic transition at 285 K accounted for only 3% of the energy taken up at 297 K (Fig. 1, bottom). These observations indicate the presence of two distinct crystalline phases, with melting points of 286 and 297 K (Höhne *et al.*, 1996), and suggest that, once formed, the phase with the lower melting point is not readily converted into the higher melting-point phase. As the transition can take place in both directions (albeit slowly for the lower melting-point phase) and the thermodynamic transition temperature appears to lie below the melting point, the system is probably enantiotropic (Dunitz & Bernstein, 1995). Since a previous accurate calorimetric study gives the melting point of pure pyrrolidone crystals as 299.082 K (extrapolated to 100% purity) (Kolesov *et al.*, 1962), we decided to investigate the nature of the lower melting-point phase formed at low temperature. We describe here its crystal structure.

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